UNIFORMED SERVICES UNIVERSITY OF THE HEALTH SCIENCES
F. EDWARD HÉBERT SCHOOL OF MEDICINE
4301 JONES BRIDGE ROAD
BETHESDA, MARYLAND 20814-4799

PREVENTIVE MEDICINE
AND
BIOMETRICS

5 June, 2006

APPROVAL SHEET

Title of Thesis: Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid Phase Microextraction for the Collection of Nerve Agent Simulant

Name of Candidate: Capt Stephen L. Boglarski
Master of Science in Public Health
Department of Preventive Medicine and Biometrics

Thesis and Abstract Approval:

Gary L Hook
Chairman: CDR Gary L. Hook, PhD — 15 June 06 — Date

Lt Col Peter T. LaPuma, PhD — 15 Jun 06 — Date

Gary A Morris
LCDR Gary A. Morris, PhD — 15 June 06 — Date

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2006		**00-00-2006 to 00-00-2006**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microextraction for the Collection of Nerve Agent Simulant	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Uniformed Services University of the Health Sciences,F. Edward Hebert School of Medicine,4301 Jones Bridge Road,Bethesda,MD,20814-4799**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT

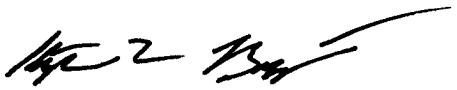
15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**94**	

The author hereby certifies that the use of any copyrighted material in the thesis manuscript entitled:

Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microectraction for the Collection of Nerve Agent Simulant

is appropriately acknowledged and, beyond brief excerpts, is with the permission of the copyright owner.



Stephen L. Boglarski, Capt, USAF, BSC
Department of Preventive Medicine and Biometrics
Uniformed Services University of the Health Sciences

ABSTRACT

Title: Application of Hydrogen Bond Acidic Polycarbosilane Polymers and Solid-Phase Microextraction for the Collection of Nerve Agent Simulant

Stephen L. Boglarski, Master of Science in Public Health, 2006

Directed By: Gary L. Hook, CDR, USN
Assistant Professor, Department of Preventive Medicine and Biometrics

Solid phase microextraction (SPME) is used to conduct analyses for trace levels of nerve agent. Measurements can be improved by using a SPME polymer coating that is selective for nerve agents in place of current commercial polymers. This research focuses on three hydrogen bond acidic polymers developed by the Naval Research Laboratory that have an increased affinity for nerve agents. These polymers were coated onto fused silica fibers using three methods: dip coating, applicator coating, and ink jet coating. Vapor and aqueous phase sampling of nerve agent simulant was conducted to evaluate the performance of these polymers. The hydrogen bond acidic polymers showed significantly higher uptakes than commercial polymers and were able to detect vapor phase nerve agent simulant at 0.005 mg/m^3 for a 1 minute sample and aqueous phase simulant at 1 ppm for a 10 minute sample. The use of these polymers with SPME extraction has the potential to provide rapid field sampling for the detection of trace levels of nerve agent.

APPLICATION OF HYDROGEN BOND ACIDIC POLYCARBOSILANE POLYMERS AND SOLID-PHASE MICROEXTRACTION FOR THE COLLECTION OF NERVE AGENT SIMULANT

By

Stephen L. Boglarski

Thesis submitted to the Faculty of the Preventive Medicine and Biometrics Graduate Program of the Uniformed Services University of the Health Sciences in partial fulfillment of the requirements for the degree of

Master of Science in Public Health

2006

Dedication

- To my wife, Amanda, for your never-ending love and support throughout our life together.
- To my parents, for the guidance you provided throughout my life and for teaching me the many reasons to strive for a good education.

Acknowledgements

I could not have accomplished this work without the help of many people and organizations. I gratefully acknowledge the support I received from:

- My thesis advisory committee: CDR Gary Hook, LtCol Peter LaPuma, and LCDR Gary Morris.
- Dr. R. Andrew McGill, Dr. Duane Simonson, and Dr. Jennifer Stepnowski from the Naval Research laboratory who facilitated the ink jet coating and provided several of the polymers used in this study.
- Dr. Eric Houser from the Department of Homeland Security who facilitated the dip coating and provided several of the polymers used in this study.
- Dr. Venkat Mani from American Analytical, who facilitated the applicator coating and provided assistance with polymer crosslinking.

Table of Contents

List of Figures

List of Tables

Introduction

1.1. Background

The field detection and identification of chemical warfare agents (CWAs) has become an increasingly critical challenge faced by today's military and civilian responders. The proliferation of WMD-related technologies and materials and the willingness of terrorist groups to obtain and employ these weapons have increased the threat of mass casualty attacks. The advent of the internet and digital mobile communications have enabled terrorist groups and rogue states to more readily acquire the technical expertise needed to develop these weapons. Terrorist groups such as Al Qaeda have openly declared their intentions to acquire and employ these weapons against civilian and military targets. In addition, factors such as the fall of the former Soviet Union have increased the probabilities that groups may attempt to steal or smuggle these weapons from nations that no longer possess tight control over their current stockpiles. (U.S. Department of State, 2006).

The use of CWAs against military and civilian populations has become an increasing realistic concern. Nerve agents, in particular, are among the most lethal CWAs. The 1995 release of the nerve agent sarin in the Tokyo subway system by the Aum Shinrikyo cult and the use of CWAs by the Iraqi Army against Kurdish refugees are both recent examples of the threat posed by these weapons (McCafferty and Lennarson, 2002). In addition to military and terrorist actions, nerve agent leakage from aging weapon storage bunkers, the decommissioning of CWA production facilities, and the demilitarization of munitions continue to pose a significant concern to human health.

Responders to any type of nerve agent incident or threat need to quickly and accurately identify the agent and to quantify the potential exposure to military and civilian personnel. Due to the lethality of these agents, field sampling techniques and equipment need to provide accurate information at trace concentrations. Although there are many different types of field sampling and detection instruments available for nerve agents, few have the accuracy and sensitivity needed to detect and quantify levels below concentrations that are immediately dangerous to life and health (IDLH). One proven technology that continues to show promise for detecting trace concentrations of nerve agents is solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (GC/MS).

1.1.1. Gas Chromatography / Mass Spectrometry (GC/MS)

GC/MS analysis is a proven technology for the analysis of volatile and semi-volatile chemicals. The GC separates the chemical components in a sample mixture. The MS is then used to identify the chemical agent by comparing the mass of the fragments in the resulting spectrum to a reference library and/or though mass spectral interpretation. The use of GC/MS for the detection and identification of CWAs has been proven to be an effective technology that is capable of identifying multiple chemicals, including nerve agents. GC/MS analysis provides both qualitative and quantitative compound-specific data, with detection sensitivities in the high parts-per-trillion (ppt) to low parts-per-billion (ppb) range (Smith et al, 2004).

1.1.2. Solid Phase Microextraction (SPME)

SPME was first developed in 1990 to address the need for simple, rapid sample preparation in a field environment. It relies on a solvent-free partitioning process that combines sampling, extraction, and concentration into a single step (Pawliszyn, 1999). SPME has been used to extract compounds directly from air and water and indirectly from soils (Harvey, 2002). SPME uses a polymeric extracting phase attached to a small fused silica fiber. The polymer extracts and concentrates chemicals from a sample matrix. The SPME fiber is then inserted directly into a GC/MS or other analytical instrument and is thermally desorbed. When coupled with GC/MS analysis, SPME provides a rapid field sampling method for the detection and identification of many chemical agents at trace concentrations (Hook, 2003a).

1.1.3. Polymer Coatings

Commercially available SPME polymer coatings are currently limited to polydimethylsiloxane (PDMS), polyacrylate (PA), or carbowax (CW) which are liquid phase polymers. These can also be combined with a solid phase polymer such as divinylbenzene (DVB) or carboxen. Each polymer differs in its adsorptive characteristics, affinity for polar and nonpolar compounds, and sensitivity and selectivity for certain analytes. Commercially available polymer coatings can concentrate and detect many CWAs (Hook, 2004), but more specialized polymers designed specifically to selectively concentrate CWAs are desirable in order to achieve lower detection limits.

The Naval Research Laboratory (NRL) has developed and tested high molecular weight sorbant polymer materials known as hydrogen bond acidic polycarbosilanes.

These polymers were used as chemical sensor coatings in CWA detection devices and were able to detect nerve agents at significantly lower airborne concentrations when compared to commercially manufactured polymers (Houser, 2004). If these hydrogen bond acidic polymers were used to make SPME fibers, they may provide lower detection limits for nerve agents when used with GC/MS analysis. These hydrogen bond acidic polymer SPME fibers could provide a rapid field collection system for first responders capable of detecting trace concentrations of these agents.

1.2. Research Question and Specific Aims

Research Question #1:

Can hydrogen bond acidic polymers be coated onto fused silica fibers and be used for SPME extraction of nerve agent simulant?

Specific Aims:

1. Test and compare three different methods for coating hydrogen bond acidic polymers onto fused silica fibers. These methods will include dip coating, applicator coating, and ink jet coating.
2. Test and compare three different hydrogen bond acidic polymers for their ability to be coated onto SPME fibers. These polymers will include the HC, FPOL, and NM_2A polymers.

Research Question #2:

Will SPME fibers coated with hydrogen bond acidic polymers have a greater collection efficiency for G-series nerve agent simulant when compared to commercially available polymers?

Specific Aims:

1. Perform vapor phase and aqueous phase sampling at multiple concentrations using SPME fibers coated with the three hydrogen bond acidic polymers and three commercially manufactured fibers.
2. Using GC/MS analysis, compare the total analyte uptake of hydrogen bond acidic polymers to that of the commercially available polymers.
3. Determine if the hydrogen bond acidic polymers can meet analyte uptake expectations established by the NRL for each type of polymer. These analyte uptake expectations compare the expected uptake of nerve agent simulant for NRL polymers in comparison with commercial PDMS.

2. Literature Review

This research brings together hydrogen bond acidic polymers and SPME to enhance field sampling and analysis techniques for nerve agents. This research will focus on G-series nerve agent simulant. Considerable research and testing has been conducted proving the effectiveness of SPME analysis of G-series nerve agents. Research has also been conducted on the effectiveness of hydrogen bond acidic polymers that demonstrates this polymer's affinity for G-series nerve agents. This chapter will provide insight on G-series nerve agents, the development of SPME and hydrogen bond acidic polymers, along with the testing conducted that provides the foundation for this thesis.

2.1. G-Series Nerve Agents

G-series nerve agents are organophosphorous compounds developed by German chemists in the 1930's and 1940's and include tabun (O-ethyl dimethylamidophosphorylcyanide (GA)), sarin (isopropyl methylphosphonofluoridate (GB)), soman (pinacolyl methylphosphonofluoridate (GD)), and GF (cyclohexyl methylphosphonofluoridate). These agents are relatively stable compounds that can be easily dispersed. The raw materials needed for their manufacture are inexpensive and to some degree readily available. Nerve agents affect the transmission of nerve impulses by inhibiting the function of the enzyme acetylcholinesterase, which is vital to the normal biological activity of the nervous system. When inhaled or absorbed through the skin, nerve agents are highly toxic and produce rapid neurotoxic effects. Death from exposure to nerve agents can result within several minutes to several hours, depending on the dose and route of exposure (Sun and Ong, 2005).

Tabun (Figure 2-1), is the easiest nerve agent to manufacture, and thus, is the most likely agent to be initially synthesized by developing nations and terrorist groups who are just starting to produce nerve agents (Sun and Ong, 2005). Tabun is an organophosphate, characterized by an oxygen phosphorous double bond, and contains a cyanide (–CN) functional group. Tabun has a moderate volatility of 328 mg/m^3 at 20° C and poses both an inhalation and skin contact hazard (Sun and Ong, 2005).

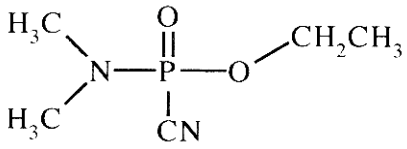


Figure 2-1. Chemical Structure of Tabun (GA)

Nations with a more mature chemical weapons program are more likely to produce sarin, soman, and GF. Sarin (Figure 2-2), differs from tabun in that it contains a fluorine atom (–F) in place of the –CN group. Sarin has a high volatility of 16,091 mg/m^3 at 20° C and poses a significant inhalation hazard (Sun and Ong, 2005).

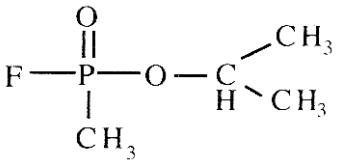


Figure 2-2. Chemical Structure of Sarin (GB)

GF (Figure 2-3), contains both the (–F) functional group and a cyclohexane ring. It exhibits a moderate volatility of 438 mg/m^3 at 20° C and poses both an inhalation and skin contact hazard (Sun and Ong, 2005).

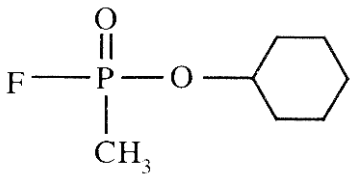


Figure 2-3. Chemical Structure of GF

Soman (Figure 2-4), also contains a fluorine (–F) functional group. It exhibits a moderate volatility of 3900 mg/m^3 at 20° C and poses both an inhalation and skin contact hazard. Soman is the most toxic of the G-series agents because it penetrates the central nervous system very quickly and irreversibly binds to acetylcholinesterase receptors in the body making medical treatment very difficult (Sun and Ong, 2005).

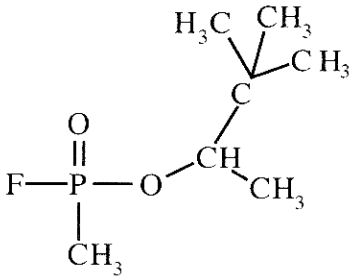


Figure 2-4. Chemical Structure of Soman (GD)

Specific airborne exposure limits for G-series nerve agents are provided in Table 2-1.

Airborne Exposure Limit	Exposure Scenario	Tabun (mg/m^3)	Sarin (mg/m^3)	Soman & GF (mg/m^3)
IDLH (Immediately Dangerous to Life and Health)	One time exposure	0.1	0.1	0.05
STEL (Short-Term Exposure Limit)	Occasional 15 minute exposure	0.0001	0.0001	0.00005
TWA (Time-Weighted Average)	Daily, 8hr, 30 year exposure	0.00003	0.00003	0.00003

Table 2-1. Airborne Exposure Limits for G-Series Nerve Agents for the U.S. Army (Department of the Army, 2004)

Due to the high toxicity and rapid mechanism of action of these nerve agents, expedient field detection is needed at trace concentrations in order to protect military and civilian populations. Traditional rapid field sampling technologies for nerve agents generally do not have the sensitivities required to detect agents at very low toxicologically relevant concentrations. These technologies also tend to have a larger footprint, less portability, and require additional logistical support. The goal of field technology development for nerve agent detection is to produce sampling and analytical instrumentation that is small, lightweight, easy to use, and provides qualitative and quantitative information for multiple chemicals while maintaining a high selectivity and sensitivity for nerve agents. The application of SPME and GC/MS offers many of these benefits for the detection of nerve agents (Hook, 2003a).

2.2. Solid Phase Microextraction

A SPME fiber usually consists of a 1 cm length of fused silica, approximately 80-125 µm in diameter, attached to a needle assembly. The fiber is coated with a small quantity of polymer. The polymer coating thicknesses ranges between 5-100 µm and serves as the extracting phase. Total polymer volume is usually less than 1 µl. Thicker polymer coatings generally lead to increased sensitivity, but require a longer sampling time (Pawliszyn, 1997). The coated fiber is housed inside a syringe-type needle that protects and isolates the fiber from exposure and can safely puncture the septum of a sample container (Figure 2-5).

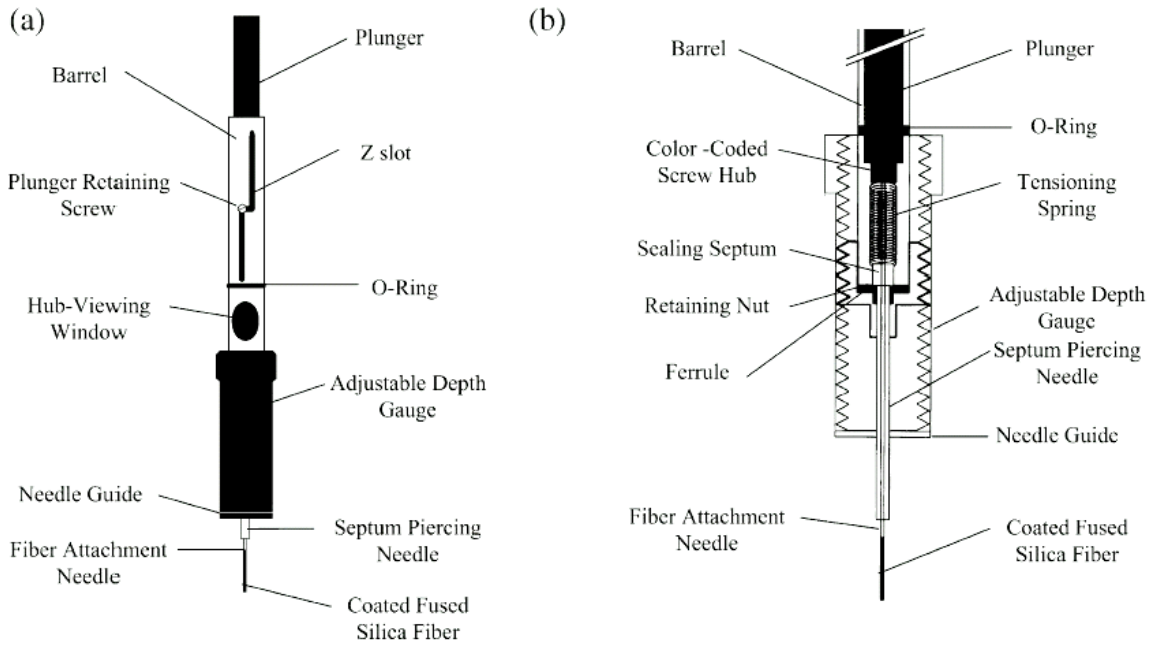


Figure 2-5. (a) SPME Fiber Holder and (b) Fiber Assembly (Bryant, 2005)

During SPME sampling, the coated fiber is extended out of the end of the needle and is exposed to a gas or a liquid for a specific period of time. During this time, volatile

and semi-volatile chemicals partition to the polymer through adsorption or absorption, depending on the type of polymer used (Pawliszyn, 1997). Since the quantity of polymer is generally very small compared to the volume of sample media, the polymer will come to equilibrium with its surroundings in a relatively short period of time. As the fiber reaches equilibrium, additional collection of analyte by the exposed fiber will not occur. When sampling is completed, the fiber is retracted back into the protective needle and sealed with a septum if it is not immediately analyzed. When used with GC/MS analysis, the retracted fiber is inserted into a heated GC injection port. The fiber is then extended out of the needle and the analytes are thermally desorbed from the fiber into the GC/MS for analysis (Pawliszyn, 1999).

The quantity of analyte extracted by a polymer at equilibrium can be determined by the partition coefficient between the analyte and the polymer coating material. Equation 2-1 describes the mass of analyte extracted by the polymer after equilibrium has been reached.

$$n = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \qquad \textbf{Equation 2.1}$$

n = analyte extracted by the polymeric phase (µg)
K_{fs} = fiber coating/sample distribution constant
V_f = fiber coating volume (m^3)
V_s = sample volume (m^3)
C_o = concentration of analyte in the sample ($\mu g/m^3$)

Equation 2-1 indicates that there is a direct proportional relationship between sample concentration and the amount of analyte extracted. When the sample volume is very large relative to the fiber coating volume ($K_{fs} V_f \ll V_s$), equation 2-1 can be simplified to:

$$n = K_{fs} V_f C_o$$ **Equation 2.2**

Equation 2.2 demonstrates that the quantity of analyte extracted can be determined independent of sample volume. It is not necessary to measure the volume of air that is sampled, which is commonly required for most traditional air sampling procedures. This makes SPME an ideal technique for field sampling (Pawliszyn, 1999).

SPME is usually considered a passive sampling technique since the fiber is simply placed into a sample matrix and chemicals partition to the polymeric phase. To collect volatile and semi-volatile compounds from soil or liquid, fibers can be exposed in air, directly immersed into a liquid, or can be placed in a container's headspace. For air sampling, the natural convection of air is generally sufficient to facilitate the partitioning of analytes to the polymer. For liquid sampling, however, a zone of depletion can form around the fibers as chemical compounds are partitioned out of the liquid. However, this can be corrected by continuously stirring the sample while the fiber is immersed in the liquid (Pawliszyn, 1999).

2.3. Solid Phase Microextraction Sampling

Rapid sampling and quantitative analysis of nerve agents using SPME and GC/MS have been demonstrated in numerous studies. Hook *et al*. (2003a) described the benefits of using SPME sampling coupled with GC/MS analysis for the detection of VX nerve agent contamination. This research found that PDMS coated fibers were capable of detecting 1.0 µg of VX per gram of soil. Schneider *et al.* (2001) established the effectiveness of SPME for rapid field detection of sarin in both air and water. This study

found a limit of detection (LOD) of 0.1 µg/L of sarin in headspace sampling and a LOD of 12 µg/L using direct immersion of the fiber into an aqueous solution. Headspace sampling of VX by Hook *et al*. (2003b) was performed to compare the performance of five commercially available polymer coatings. Results showed that the PDMS, PA, CW/DVB, and PDMS/DVB polymers provided similar uptake kinetics. Lasko and Ng (1997) demonstrated the effectiveness of SPME and GC/MS in detecting 60 ppb of sarin, soman, tabun, and VX in samples of tap water, river water, sea water and sewage. The detection of airborne sarin using both static and dynamic SPME was studied by Hook *et al*. (2004). A dynamic system where contaminated air was pumped across a SPME fiber inside a sampling chamber demonstrated that more sarin was captured in comparison to a static sampling system. The success of these studies shows that SPME sampling, when coupled with GC/MS analysis, is an effective method for the detection and quantification of nerve agents in many different sample media.

2.4. Polymer Coatings

Commercially available polymer coatings for SPME fibers differ in their mechanism of extraction (absorption or adsorption), and in their affinity for polar or nonpolar analytes. Coatings are classified into two separate types: 1) homogenous pure polymer coatings and 2) porous particles embedded in a polymeric phase. There are two commercially available homogenous pure polymer coatings that have absorptive characteristics. Polydimethylsiloxane (PDMS) has a high affinity for nonpolar analytes and is the most widely used general purpose polymer. Polyacrylate (PA) possesses an affinity for polar analytes. The remaining polymer coatings use a mixed phase system

containing porous particles, either divinyl benzene (DVB) or carboxen, embedded in a partially cross-linked polymeric phase, either PDMS or carbowax (CW). These mixed phase polymers have adsorptive characteristics and have a higher selectivity and sensitivity for certain analytes (Pawliszyn, 1999).

Recent research and development has yielded new polymers that have hydrogen bond acidic functional groups. These functional groups are characterized by an electron deficient hydrogen atom that allows the polymer to extract analytes by chemisorption rather than adsorption. It can also increase selectivity towards specific analytes as well as improve sensitivity. These qualities offer a distinct advantage over commercially available polymers. PDMS, for example, is a highly viscous linear chained polysiloxane and does not have hydrogen bond acidic functional groups (Figure 2-6). It absorbs most nonpolar substances and, therefore, cannot target specific analytes (Pawliszyn, 1999).

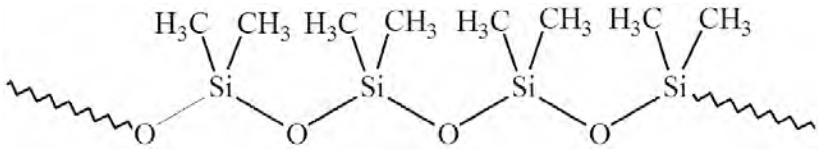


Figure 2-6. Chemical Structure of Linear PDMS Polymer

The NRL has recently developed and tested hydrogen bond acidic polymers characterized by fluoroalcohol-substituted polycarbosilane chains. The basic structure of the hydrogen bond acidic polymer designated as HC is shown in Figure 2-7.

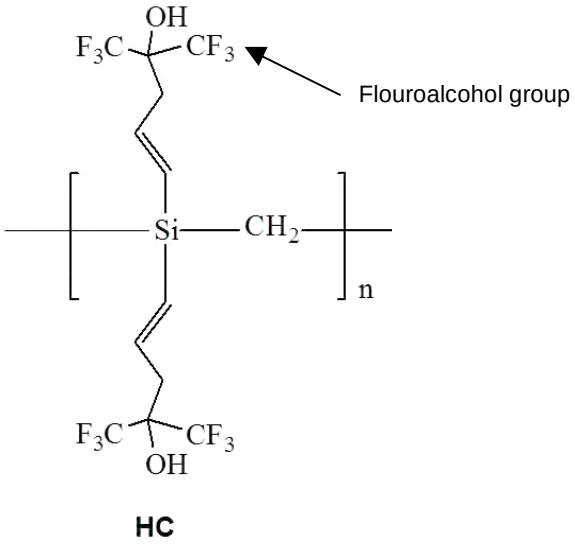


Figure 2-7. Basic Chemical Structure of HC

The carbosilane backbone offers thermal stability while the fluoroalcohol functional end groups have an electron withdrawing effect on the oxygen atom in the O-H group, thus making them hydrogen bond acidic. The absence of hydrogen bond basic sites in the polymer backbone, such as the oxygen atoms contained in linear PDMS, reduces hydrogen bonding internal to the molecule. This increases the number of fluoroalcohol groups available for hydrogen bonding with hydrogen bond basic analytes such as organophosphates and nerve agents and leads to higher uptake of these agents (Bryant, 2005). Hydrogen bond acidic polymers can be either linear or hyperbranched. While the two types perform similarly in regards to their uptake of nerve agent, the linear polymers are generally more viscous and have a higher molecular weight than the hyperbranched polymers (NRL, 2006).

The vapor sorptive properties of hydrogen bond acidic polymers were evaluated by Houser *et al.* (2004) in surface acoustic wave (SAW) sensors. Results showed that these polymers had a high sensitivity to hydrogen bond basic vapors such as the nerve

agent simulant dimethyl methylphosphonate (DMMP). DMMP is hydrogen bond basic at the terminal oxygen atom of the P=O bond. The bonding mechanism between the HC polymer and DMMP is shown in Figure 2-8. Previous experimentation by the NRL shows that HC will absorb an average of 20 times more nerve agent as compared to commercial PDMS (NRL, 2006).

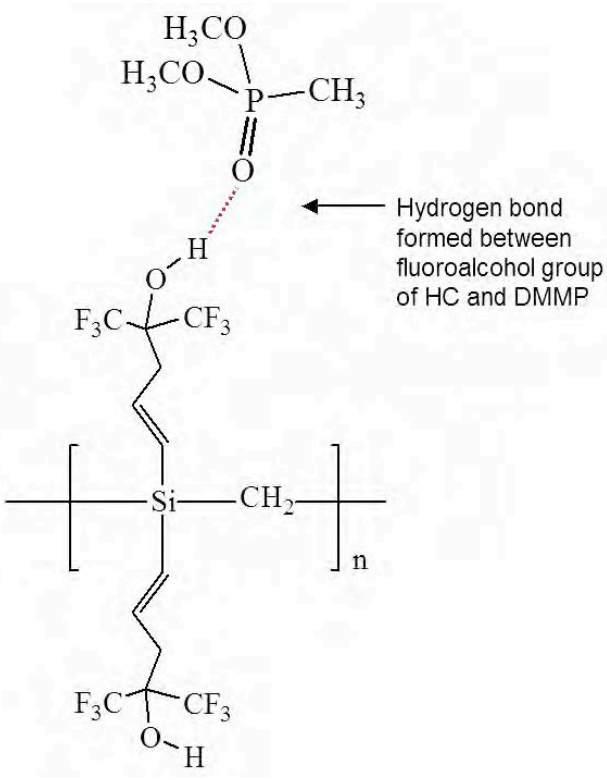


Figure 2-8. Hydrogen Bonding Between HC and DMMP (Bryant, 2005)

Another polymer currently being tested by the NRL is FPOL (Figure 2-9). This polymer is also characterized by multiple fluorocarbon and O-H functional groups.

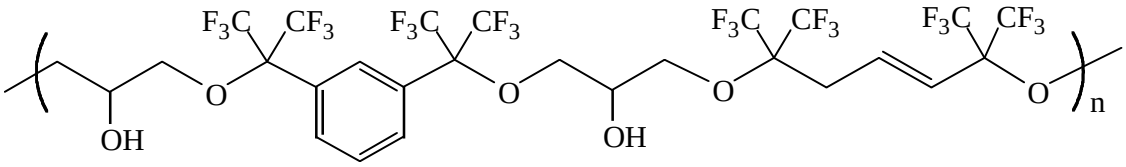


Figure 2-9. Basic Chemical Structure of FPOL

Unlike the HC polymer, FPOL is a fluoro-ether where the O-H groups are not located next to the Fl groups but are connected to the polymer backbone. FPOL also has oxygen groups within the polymer backbone. Due to this configuration, FPOL should still have an affinity for hydrogen bond basic analytes, but will not be nearly as selective as HC. Previous experimentation shows that FPOL will absorb an average of 2-3 times more nerve agent as compared to commercial PDMS. FPOL also has a lower molecular weight and lower viscosity than HC (NRL, 2006).

The NM_2A polymer is another hyperbranched hydrogen bond acidic polycarbosilane that is being tested by the NRL (Figure 2-10). NM_2A is a linear polymer

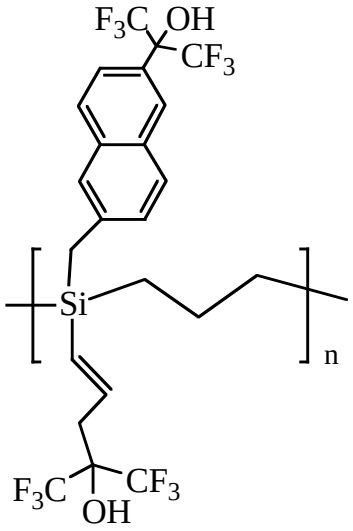


Figure 2-9. Basic Chemical Structure of NM_2A

with a carbosilane backbone and fluoralcohol groups attached to naphthlylmethyl groups. As with the HC polymer, the fluoroalcohol groups create strong hydrogen bond acidity. The increased electron density due to the aromatic naphthyl rings may increase the interaction between the polymer and target analytes. NM_2A has a higher molecular weight and viscosity than HC due to the napthyl rings but has fewer fluroaclohol end groups. Previous experimentation by the NRL has shown that it can absorb, on average, ten times the amount of nerve agent simulant when compared to commercial PDMS (NRL, 2006).

Further comparison studies by other researchers have shown that hydrogen bond acidic polymers exhibit a significantly higher selectivity to nerve agent simulants relative to general purpose polysiloxane polymers. Houser *et al.* (2004) demonstrated that fluoroalcohol substituted polycarbosilanes have higher sensitivity toward nerve agent simulant due to the absence of hydrogen bond basic sites (oxygen atoms) within the polymer backbone. Grate *et al*. (1993) also demonstrated that hydrogen bond acidic polymers provide a high selectivity and sensitivity for nerve agent simulants and actual nerve agents. Pacific Northwest National Laboratories (PNNL) designed several polymers that consisted of hydrogen bond acidic hexafluorobisphenol groups between polydimethylsiloxane spacers. The PNNL polymers were tested by Grate *et al.* (1999) in SAW vapor sensors and the results showed they provided better detection of trace concentrations of organophosphates when compared to commercially available polymers. Harvey *et al.* (2002) coated SPME fibers with a phenol-based hydrogen bond acidic polycarbosilane polymer and evaluated its selectivity towards sarin as compared to

standard PDMS polymers. This study showed the hydrogen bond acidic polymer exhibited a 20-fold higher uptake of sarin than PDMS, coupled with a lower selectivity towards total hydrocarbons. Overall, these studies have shown the use of hydrogen bond acidic polymers can provide superior uptake for selected analytes such as nerve agents. Successfully coating SPME fibers with the hydrogen bond acidic polymers developed by the NRL will allow samples to be rapidly collected and analyzed on a GC/MS with a SPME injection port.

3. Methodolgy

This chapter describes the methods used to answer the research questions discussed in Chapter 1. The first objective of this research was to determine if the hydrogen bond acidic polymers can be effectively coated onto SPME fibers and to test three different coating methods. Dip coating, applicator coating, and ink jet coating methods are examined. The second objective was to test the coated fibers against known concentrations of nerve agent simulant and compare the performance of the hydrogen bond acidic polymers to commercially available polymers and to analyte uptake expectations established by the NRL for each type of polymer. Two methods of simulant sampling were tested: static vapor phase sampling and direct immersion aqueous phase sampling.

3.1. Application of Polymer Coatings

3.1.1. Dip Coating

Dip coating was the first method tested for applying hydrogen bond acidic polymers to SPME fibers. The dipping solutions were prepared by dissolving a selected quantity of HC polymer and an adhesive PDMS polymer in a methylene chloride (Aldrich Chemical Co., Cas#75-09-2) solvent along with a platinum catalyst. The low viscosity of the HC polymer made it unsuitable for coating the fiber using only the neat polymer as it did not adhere to fiber. Therefore, the adhesive PDMS polymer was added to the HC polymer to both increase the viscosity of the mixed solution and promote crosslinking within the polymer matrix. The adhesive PDMS polymer is a linear PDMS,

with 5-7% of its functional groups being Si-H groups (Figure 3-1). These silicon-bonded hydrogen atoms readily crosslink the chains of the PDMS polymer with other PDMS chains and with the chains of the HC polymer in the presence of a platinum catalyst.

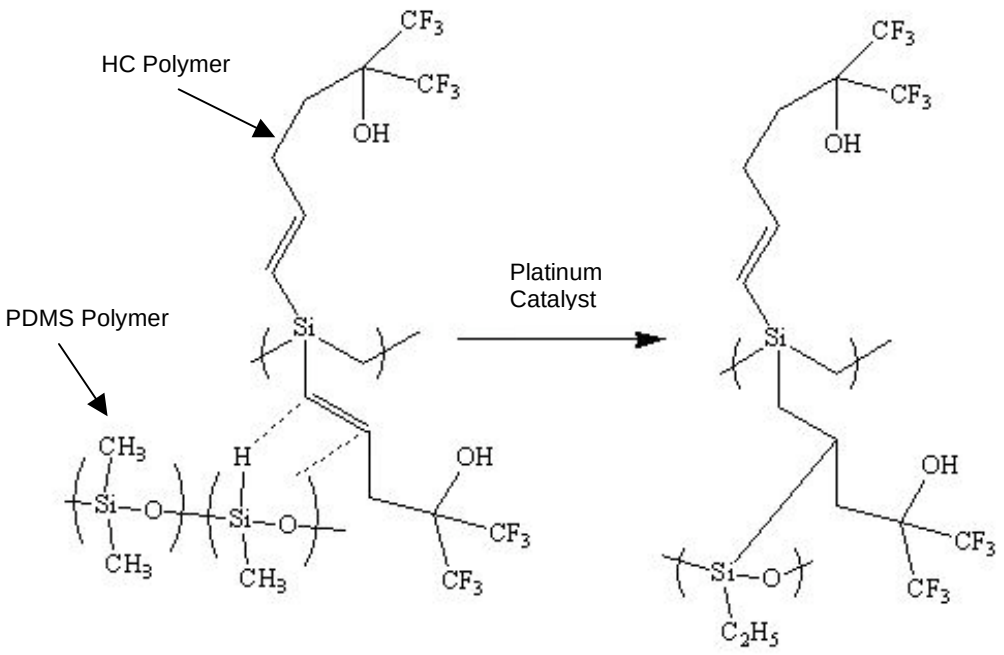


Figure 3-1. Crosslinking of PDMS and HC Polymer Chains

The catalyst is a platinum (0)-2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane complex solution (Aldrich Chemical Co., Cas#68585-32-0). In order to achieve the appropriate amount of crosslinking needed to stabilize both polymers in a solid matrix, the HC polymer was combined with the adhesive PDMS polymer in a 50/50 mixture by weight.

The first step in creating the dipping solution involved adding 250 mg of the HC polymer to a glass vial. A microbalance (Sartorius, model BP-615) was used to weigh the appropriate amount. An equal mass of the adhesive PDMS polymer was then added

to the vial. The next step involved adding a selected quantity of methylene chloride. Three separate dipping solutions were created by adding 1.0, 2.0, or 3.0 ml of methylene chloride. This was done to determine which concentration would result in the best coating. Once the polymers were fully dissolved in the solvent (approximately 30 minutes), 5.0 µl of platinum catalyst was added to the vial to initiate crosslinking. The mixed polymer solution was stirred until a uniform viscosity was achieved. The vial was then secured to a laboratory stand in preparation for dip coating.

Standard Supelco fiber assemblies with uncoated fused silica fibers, 1 cm in length and 110 µm in diameter, were used for the dip coating. The fiber assembly was placed in a standard Supelco SPME fiber holder, and the fiber was extended out of the assembly. The fiber was then repeatedly dipped, 3-6 times, into the polymer solution until a visible coating was achieved. The fiber was then removed from the solution and was held horizontally and rotated to prevent the polymer from collecting at one end of the fiber and ensure a more even distribution of the coating along the fiber. The fiber was rotated for 30 seconds while the solvent evaporated. This dipping and evaporation process was then repeated 2-3 additional times until a semi-uniform coating was present along the entire length of the fiber.

A problem with this method involved the tendency of the polymer to clump together in beads on the surface of the fiber instead of attaching as a smooth coating as seen in commercial polymer coatings. The beads of polymer were manually smoothed by using a second uncoated fiber like a paint brush to break up the beads and spread the polymer along the surface of the fiber. This helped to improve the uniformity of the polymer coating.

The fiber was then partially cured by placing it in a vacuum oven (Cole Parmer, StableTemp) at 100° C under a vacuum of 20 in. Hg for 30 minutes. This was done to evaporate any remaining solvent and to promote polymer crosslinking. A vacuum pump (GE, model 5KH36KNA510X) was used to create the vacuum. After removal from the oven, the fiber was re-dipped in the solution using the same dipping procedures to add an additional layer of polymer to the fiber. Some additional beading of the polymer was observed and the beads were again manually smoothed. The target polymer thickness was 30 µm. This thickness was chosen to make it comparable with a commercial 30 µm PDMS fiber. After the final dip coated layer, the fiber was hardened by placing it in the vacuum oven for 16 hours at a temperature of 120° C and 20 in. Hg pressure.

The dipping solution that contained the 3.0 ml of methylene chloride was found to be too dilute and did not result in any of the polymer mixture adhering to the fiber. The dipping solutions with 1.0 ml and 2.0 ml of methylene chloride resulted in semi-uniform polymer coatings. The fibers created from these dipping solutions were used for vapor and aqueous phase sampling and are designated as fibers "HC/PDMS (Dipped#1)" and "HC/PDMS (Dipped#2)" respectively.

3.1.2. Applicator Coating

Applicator coating was performed with assistance from Dr. Venkat Mani, American Analytical, State College, PA. Both the HC and FPOL polymers were selected for applicator coating. For coating with the HC polymer, a 50/50 mixture of the HC and the adhesive PDMS polymer was used. First, 6.0 ml of methylene chloride was added to a glass vial. Then 750 mg of the HC polymer and 750 mg of the adhesive PDMS

polymer were added to the vial and allowed to dissolve into solution. After approximately 30 minutes, 15.0 µl of the platinum catalyst (same as with dip coating) was added to the vial to initiate the crosslinking process. The mixed polymer solution was then stirred until a uniform viscosity was achieved.

A 12 inch long uncoated fiber made of fused silica polyacrolate (FSA) (Polymicro Technologies, FSA080120) was used for the applicator coating. The FSA fiber had a fused silica diameter of 83 µm with a 21 µm thickness of polyacrolate for a total fiber diameter of 125 µm. The polyacrolate coating strengthened the silica fiber and provided a favorable surface for attaching the polymer. The FSA fiber was first pretreated by dipping it in a methylene chloride solution for 20 seconds. Approximately 4.0 ml of the mixed polymer solution was poured into a funnel-shaped silicon applicator. The end of the fiber was inserted into the top of the applicator and drawn out the bottom through the small end of the funnel (Figure 3-2).

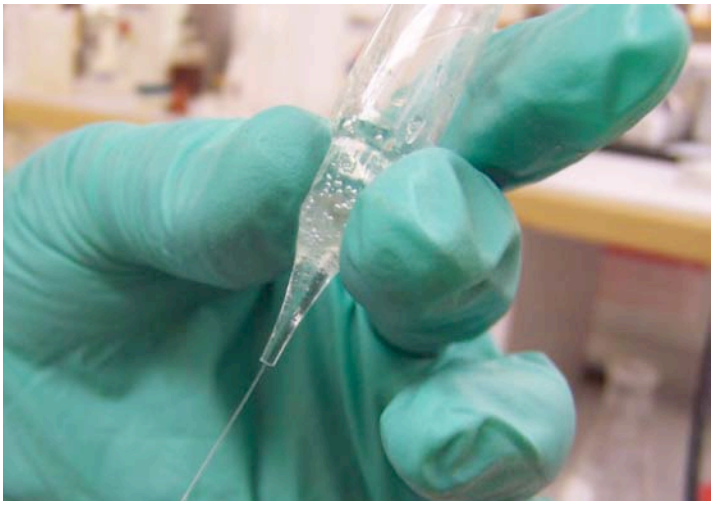


Figure 3-2. Polymer Application Using Silicon Applicator

The entire fiber was pulled through the applicator, applying a uniform coating of the polymer mixture along the FSA fiber approximately 10 μm in thickness. The fiber was then held in front of a desktop flameless heater for 2 minutes to enhance evaporation of the methylene chloride solvent and crosslinking of the polymer matrix. The fiber was passed through the applicator and heated in the same manner a total of 4 times in order to add additional layers of polymer to the FSA fiber and bring the total polymer thickness to approximately 40 μm.

The coated fiber was then placed in an oven (Blue M, Stabil-Therm) inside a glass cylinder containing a nitrogen atmosphere. It was cured at 200° C for 16 hours in order to evaporate the remaining methylene chloride and promote additional crosslinking of the polymer mixture. A nitrogen atmosphere was used to prevent degradation of the PDMS polymer that could occur in the presence of oxygen. The fiber was then removed from the oven and allowed to cool to room temperature. The fiber was then cut into 2 cm lengths. Each length of fiber was inserted 1 cm into the needle of a standard Supelco SPME fiber assembly and glued into place. This allowed 1 cm of the fiber to be exposed for sampling. The entire process was then repeated using the FPOL polymer combined in a 50/50 mixture of FPOL and adhesive PDMS. The fibers created from these mixtures and used in further vapor and aqueous phase testing are designated as fibers “HC/PDMS (Applicator)” and “FPOL/PDMS (Applicator)”.

3.1.3. Ink Jet Coating

The third method evaluated in this study is the ink jet coating method. This method was performed in conjunction with the NRL using a Jet Lab II (Microfab

Technologies, Inc.) ink jet printing platform. The goal of the ink jet coating method was to produce a fiber with a more uniform polymer coating that could be easily replicated. The two coatings chosen for the ink jet coating method were the HC and NM_2A polymers. The NM_2A polymer was chosen in place of the FPOL polymer since the NM_2A has a higher molecular weight and higher viscosity which would make it easier to coat onto a SPME fiber.

Standard Supelco fiber assemblies with uncoated fused silica fibers, 1 cm in length and 110 µm in diameter, were used for the ink jet coating method. The uncoated fused silica fiber was inserted into a standard SPME fiber holder which was then secured to an aluminum holder. The fiber was positioned on the stage of the ink jet printing platform so that the fiber was situated approximately 3mm directly below the ink jet nozzle and 2 cm above the heated stage as shown in Figure 3-3. For all ink jet coatings,

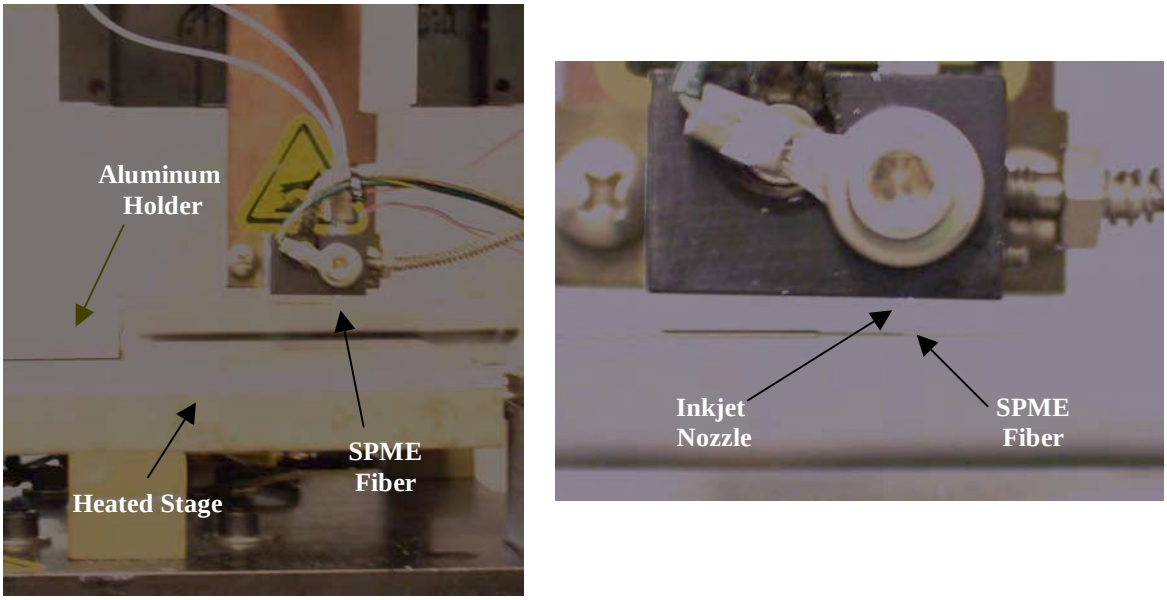


Figure 3-3. Ink Jet Coating Set-Up

the stage was heated to 110 ^{o}C to aid in solvent evaporation as the droplets were dispersed and adhered to the fiber.

The HC polymer was first dissolved in a butanol solvent in order to decrease its viscosity prior to jetting. This was done to ensure that the polymer solution would not clog the ink jet nozzle. A solution of 1.0% HC polymer (by weight) in 1-butanol (CAS#71-36-3, Aldrich Chemical Co.) was used. The 1.0% HC polymer solution was then loaded into the well of the ink jet nozzle.

Eight layers of the HC coating were applied to the uncoated fused silica fiber. The specific ink jet settings used for the formation of the droplets and the coating pattern are given in Appendix A. The first layer of polymer was applied to the fiber by jetting 100 bursts along the entire l cm length of the fiber in two parallel rows for a total of 200 bursts. The fiber remained stationary. Each burst contained 200 droplets of the polymer solution. Each droplet was approximately 100 μm in diameter. While coating the first layer, formations of combined droplets appeared as small beads of polymer on the fiber. These small beads moved along the fiber due to capillary action and surface tension. The beads became larger as they moved along the surface of the fiber and collected additional droplets of polymer.

The second layer of polymer coating was then applied to the HC fiber approximately two minutes after the first layer. For the second layer, the coating pattern was expanded to three parallel rows to maximize the amount of solution deposited on the fiber. At 100 bursts per row, this increased the total number of bursts to 300. The third and fourth layers were also coated onto the fiber using the three parallel rows and 300 total bursts.

The fiber was then rotated 180 degrees to apply an additional four layers to the opposite side of the fiber. For the fifth layer (the first just after the fiber rotation), the spacing between each burst was doubled to reduce large bead formation. Therefore, the number of bursts in each row was reduced from 100 to 50 bursts for a total of 150 bursts. Increasing the burst spacing did not appear to reduce the capillary effect. For the sixth, seventh and eighth layers, the same three rows at 150 total bursts were maintained but the number of droplets per burst was reduced. The droplets were reduced from 100 to 50 to 25 drops per burst, respectively. The lower burst rates were found to reduce large bead formation and their movement along the fiber. The HC fiber created from the ink jet coating method and used in further vapor and aqueous phase sampling is designated as fiber "HC (Ink Jet)".

A second fused silica fiber was coated using the NM_2A polymer. A jetting solution of 0.4% NM_2A polymer (by weight) in a 20/80 mixture (by weight) of toluene (CAS#108-88-3, Aldrich) and 1-butanol was used. The 0.4% concentration of NM_2A polymer and the mixture of the two solvents had to be used to achieve complete dissolution of the NM_2A in the solvent.

A total of 16 layers (8 per side) of NM_2A polymer were applied to the fiber using a burst rate of 50 droplets per burst. Three parallel rows were again applied for each layer but the distance between each burst was increased which resulted in 44 bursts per row (instead of 50) for a total of 132 bursts per layer (instead of 150). The fiber created from ink jet coating the NM_2A solution and used in further vapor and aqueous phase sampling was designated as fiber "NM_2A (Ink Jet)". Microscopic images and further

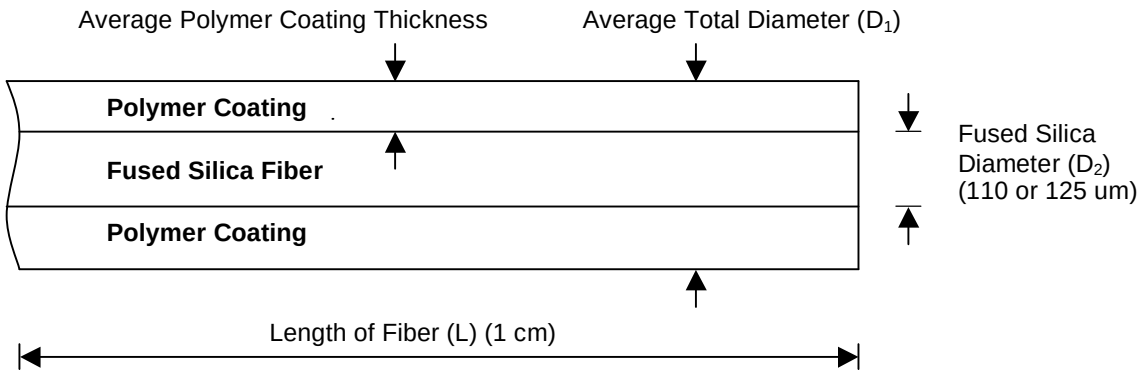
analysis of all ink jet coated fibers are given in section 4.1.3. The ink jet settings used for droplet formation and the coating pattern are given in Appendix A.

3.2. Fiber Imaging

Measurement of the polymer thickness of each fiber was made by imaging each fiber under a Leica Model DM LB microscope using the 20X magnification lens. The fiber to be measured was inserted into a SPME fiber holder, which was then secured to a laboratory stand. The position of the fiber on the stand was adjusted so that the SPME fiber holder laid flat on the microscope stage. It was supported by four stacked glass slides to ensure that the distance from the lens was always the same and repeatable measurements could be achieved. The microscope was focused so the edges of the fiber were clear. This ensured that the depth of the focus was half way into the fiber. A video image of the fiber under the 20X magnification lens was then captured using the microscope's camera (QImaging, Micropublisher) and imaging software (QImaging, QCapture 1394) and displayed on a computer screen.

Using the Image-Pro Discovery software, a measurement of the total fiber diameter of an uncoated Supelco fused silica fiber was made using the software's built-in measurement tools. This procedure optically calibrated the measurement tool. Images of the test fibers were obtained using the same procedures and total fiber diameter measurements were obtained. Ten measurements were taken every 1mm along the length of the polymer coating in order to obtain an average fiber diameter. Average polymer coating thickness was obtained by subtracting the diameter of the uncoated fused silica fiber (either 110 or 125 um) from the average total fiber diameter and dividing by two.

The total volume of polymer coating was then determined by calculating the total combined volume of both the polymer coating and fused silica fiber and subtracting the volume of the fused silica fiber (Figure 3-4).



$$\text{Average Polymer Coating Thickness} = (D_1 - D_2) / 2$$

$$\text{Total Polymer Coating Volume} = \pi (D_1 / 2)^2 L - \pi (D_2 / 2)^2 L$$

Figure 3-4. SPME Fiber Measurements

Microscopic fiber imaging was also used to visually analyze the overall quality of and uniformity of the polymer coatings. Digital photographs of the test fibers were taken both before and after sampling was performed to determine if the polymer coatings had been damaged or degraded through repeated vapor and aqueous phase sampling.

3.3. Nerve Agent Simulant

Nerve agent simulants are chemicals that are produced in order to mimic the behavior of actual nerve agents. Simulants have similar structure and functional groups

as nerve agents. Simulants also have similar physical properties such as vapor pressure and ionization affinity. The major advantage of using nerve agent simulants is that they are much less toxic and easier to work with. Dimethyl methylphosphonate or DMMP (97%, Aldrich Chemical Co., CAS# 756-79-6) was the simulant selected due to its structural similarities to military nerve agents and the many organophosphate based chemicals and pesticides used in industry (Figure 3-9). DMMP was used for both vapor phase and aqueous phase sampling.

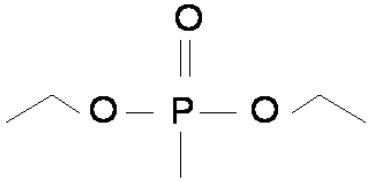


Figure 3-5. Basic Chemical Structure of DMMP

3.4. Vapor Phase Extraction

The six different SPME fibers coated with the hydrogen bond acidic polymers discussed in the previous sections were tested using static vapor phase extraction from tedlar bags. Three commercially manufactured fibers were used for comparison for a total of nine test fibers. The three commercial fibers included two PDMS fibers with coating thicknesses of 30 μm and 7 μm and a DVB/PDMS fiber with a 65 μm thickness. The PDMS fibers were tested to give a basis of comparison between the hydrogen bond acidic polymers and general purpose commercial polymers of similar thickness. The DVB/PDMS (65μm) fiber was used due to the fact that previous research (Lasko, 1997) has shown that this coating gave much higher GC/MS peak areas when compared to other

commercial polymers for the aqueous phase extraction of sarin. Table 3-1 shows all of the polymers that were tested using vapor phase extraction.

Fiber	Coating Method
Dip Coated	HC/PDMS (Dipped #1)
	HC/PDMS (Dipped #2)
Applicator Coated	HC/PDMS (Applicator)
	FPOL/PDMS (Applicator)
Ink Jet Coated	HC (Ink Jet)
	NM2A (Ink Jet)
Commercially Manufactured	PDMS (30um)
	PDMS (7um)
	DVB/PDMS (65um)

Table 3-1. Test Fiber Information

3.4.1. Sample Preparation

To compare the uptake of vapor phase simulants for each of the test fibers, known concentrations of DMMP were created in a 5.0 L tedlar bag (SKC). DMMP concentrations of 0.5, 0.05, and 0.005 mg/m^3 were selected to challenge each of the polymers against concentrations that would compare to the IDLH values of G-series nerve agents (0.05-0.1 mg/m^3).

The 5.0 L tedlar bag was filled with 4.0 L of ambient air using a 2.0 L macro-volume syringe (SGE Inc.). In order to achieve the 0.5 mg/m^3 concentration in the bag, a stock solution of 2.0 mg/ml DMMP in methylene chloride was mixed in a 15 ml silanized glass vial. One microliter of the stock solution was drawn from the vial using a 10.0 ul

syringe (Hamilton, #701), and injected into the tedlar bag through its PFTE-lined silicone septa. A solvent chase method was used to draw the stock solution, where 1.0 µl of methylene chloride was drawn into the syringe, followed by 1.0 µl of air, followed by the 1.0 µl of stock DMMP solution, followed by an additional 1.0 µl of air. This method was used in order to ensure that 1.0 ul of the stock solution was accurately injected into the bag. After injection of the DMMP stock solution, the bag was allowed to equilibrate for 30 minutes. The bag was then purged using a high flow pump (Gilian, model 800485). This process was repeated two additional times to minimize loss of analyte to the walls of the tedlar bag. After the third evacuation, the bag was filled to the desired concentration for sample collection. To achieve the 0.05 and 0.005 mg/m^3 concentrations in tedlar bags, stock solutions of 0.2 and 0.02 mg/ml DMMP in methylene chloride were used.

3.4.2. SPME Sampling Protocol

The hydrogen bond acidic test fibers were conditioned at 120° C for 30 minutes prior to use. This temperature was recommended by the NRL to minimize the chance for degradation of these polymers. All commercial test fibers were conditioned at 250° C for 30 minutes according to the manufacturer's recommendations. Sampling was conducted at ambient room temperature. The fiber to be tested was first inserted into a SPME fiber holder. Then the septum of the tedlar bag was pierced with the SPME fiber needle and the fiber was extended inside the bag. A standard extraction time of 10 minutes was used. Longer sampling times are generally undesirable in field sampling conditions. After 10 minutes, the fiber was retracted back into the needle and the SPME sampler was removed from the bag. The fiber was then promptly inserted into a heated

GC injection port. The fiber was extended into the mid-range region of the injection port liner and GC/MS analysis was conducted.

Triplicate samples of the test fibers listed in Table 3-1 were obtained at the 0.5 and 0.05 mg/m^3 test concentrations. Hydrogen bond acidic polymers that showed a significantly higher analyte uptake per μm^3 of polymer volume versus commercial polymers at the 0.05 mg/m^3 concentration were then challenged at 0.005 mg/m^3 along with the two commercial PDMS fibers for comparison. Triplicate samples of these fibers were obtained using both 10 and 1 minute sampling times. The 1 minute extractions were performed in order to determine if this shorter extraction time would still be sufficient to detect the analyte of interest at the lowest test concentration.

3.5. Aqueous Phase Extraction

Direct immersion sampling was used to test the uptake of DMMP in an aqueous phase. The same six hydrogen bond acidic fibers and three commercial fibers that were tested during the vapor phase sampling were also used for aqueous phase sampling (Table 3-1).

3.5.1. Sample Preparation

For aqueous phase sampling, test concentrations of 100 ppm and 1 ppm DMMP in water were created. To prepare the 100 ppm concentration, a stock solution of 10% DMMP in methylene chloride was mixed by adding 0.5 ml of DMMP to 4.5 ml of methylene chloride in a silanized glass vial. From this stock solution, 1.2 µl was extracted and injected into a separate vial containing 12.0 ml of deionized water. This

resulted in a final concentration of 100 ppm DMMP. A solvent chase method was again used to ensure accuracy and reproducibility of the injections. To prepare the 1.0 ppm concentration, a stock solution of 0.1% DMMP in methylene chloride was mixed by adding 0.1 ml of DMMP to 9.9 ml of methylene chloride in a silanized glass vial. From this stock solution, 1.2 µl was extracted using a 10.0 µl syringe and injected into a separate vial containing 12.0 ml of deionized water to create the final concentration of 1 ppm DMMP. Each test vial was placed on a magnetic stirrer (Barnant Co., model 700-5011) and mixed for 30 minutes prior to sampling.

3.5.2. SPME Sampling Protocol

The hydrogen bond acidic test fibers were conditioned at 120° C for 30 minutes prior to use. This temperature was recommended by the NRL to minimize the chance for degradation of these polymers. All commercial test fibers were conditioned at 250° C for 30 minutes according to the manufacturer's recommendations. Sampling was conducted at ambient room temperature. The fiber to be tested was first inserted into a SPME fiber holder. Then the septum of the test vial was pierced with the SPME fiber needle and the fiber was extended into the vial so that the entire length of the exposed fiber was immersed in the liquid. The liquid in the vial was continuously stirred during sampling using a magnetic stirrer. An extraction time of 10 minutes was used. After 10 minutes the fiber was retracted back into the needle and removed from the vial. The SPME fiber was then promptly inserted into a heated GC injection port. The fiber was extended into the mid-range region of the injection port liner and GC/MS analysis was

conducted. Triplicate samples of the nine of the test fibers were obtained at both the 100 ppm and 1 ppm test concentrations.

3.6. GC/MS Analysis

GC/MS analysis of the SPME samples were performed using an Agilent GC with a noncoated inert electron impact ionization source and monolithic hyperbolic quadrapole mass selective detector. The GC used a 30m x 0.25 mm I.D. DB5-MS column having a film thickness of 0.25 μm. Helium at a linear velocity of 1.4 ml/min and constant flow was be used as the carrier gas. The oven was programmed to hold at 40° C for 2 minutes and then increase to 250° C at 20° C per minute. Desorption of the SPME fiber samples was accomplished in the splitless injection mode. A 0.75 mm deactivated glass injection port liner (Supelco) was used and the injector temperature was maintained at 150° C throughout the analysis. The MS transfer line was held at 270° C. Mass spectra were collected over the range of 30-250 mass-to-charge (m/z). Sample mass spectral information was stored and analyzed using the Agilent Chemstation software package. Blank samples were run, at a minimum, once per day prior to the start of SPME samples.

3.7. Polymer Comparison and Data Analysis

The relative standard deviation (RSD) between the triplicate samples for each test fiber at each sampling concentration was calculated to analyze the reproducibility of the measurements. The total uptake (total GC/MS peak area) of DMMP as well as total uptake per μm^3 of polymer volume for each fiber was compared using a one-way analysis of variance (ANOVA) followed by a Tukey HSD Post Hoc comparison test.

Comparisons were made between the test fibers to determine which polymer and coating method gave the best performance at each sampling concentration. Results for the hydrogen bond acidic polymers were also compared with results from prior testing by the NRL that provide expected DMMP uptake for each polymer type. These uptake expectations are given in Table 3-2 and detail the average advantage in DMMP uptake that the polymer is expected to provide when compared to a PDMS fiber of equal

Polymer	Expected Advantage in DMMP Uptake
HC	20 fold
HC/PDMS (50/50 mixture)	10 fold
FPOL/PDMS (50/50 mixture)	1.5 fold
N_2MA	10 fold

Table 3-2. Expected Advantage in DMMP Uptake of Hydrogen Bond Acidic Polymers Over a PDMS Polymer of Equal Thickness

polymer thickness. In addition, previous research of the hydrogen bond acidic polymers has found that the expected advantage in DMMP uptake should be higher at lower concentrations (NRL, 2006).

4. Experimental Results and Discussion

4.1. Application of Polymer Coatings

The results from the three coating methods (dip coating, applicator coating, and ink jet coating) will be discussed in the following sections.

4.1.1. Dip Coating

Dip coating was performed using the HC polymer as described in chapter 3.1.1. The addition of the adhesive PDMS polymer and the platinum catalyst provided crosslinking and a bonded polymer coating. A microscopic image of a commercially manufactured PDMS (30μm) fiber under the 10X magnification lens is shown in Figure 4-1. Images of the HC/PDMS (Dipped#1) and HC/PDMS (Dipped#2) fibers are shown in Figures 4-2 and 4-3 respectively.

The polymer coatings of the HC/PDMS (Dipped#1 and #2) fibers were not as uniform as commercial fibers, exhibiting a slight variability in thickness along the length of the fiber. The coating of the HC/PDMS (Dipped#2) fiber was created with the more dilute dipping solution (250 mg polymer per 1.0 ml methylene chloride) which led to a slightly thinner but more uniform coating than the HC/PDMS (Dipped#1) fiber that used the thicker dipping solution (250 mg polymer per 2.0 ml methylene chloride). Both coatings fully hardened into a solid matrix and were firmly bonded to the fused silica fibers.

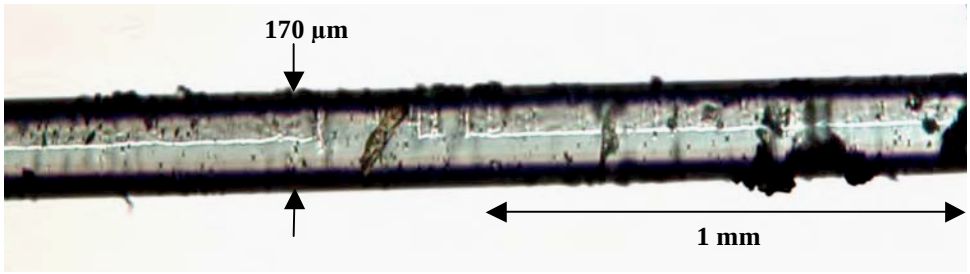


Figure 4-1. Commercial PDMS (30µm) Fiber (10X Magnification)

Figure 4-2. HC/PDMS (Dipped#1) Fiber (10X Magnification)

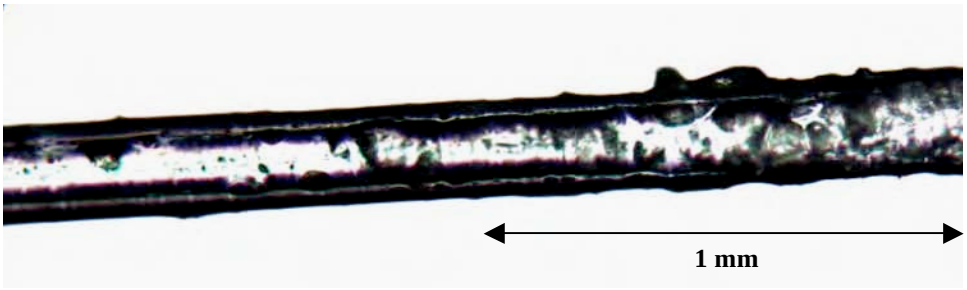


Figure 4-3. HC/PDMS (Dipped#2) Fiber (10X Magnification)

4.1.2. Applicator Coating

Applicator coating was performed using the HC and FPOL polymers, combined with the adhesive PDMS polymer as described in chapter 3.1.2. The fibers created through the applicator coating method are shown in Figures 4-4 and 4-5.

Figure 4-4. HC/PDMS (Applicator) Fiber (10X Magnification)

Figure 4-5. FPOL/PDMS (Applicator) Fiber (10X Magnification)

Both fibers were able to be fully hardened into a solid matrix and bonded to the surface of the fused silica fiber. However, there were variations in the quality of each polymer coating. The HC/PDMS (Applicator) fiber exhibited a very smooth and uniform coating. The FPOL/PDMS (Applicator) fiber coating was less uniform, having slight variations in thickness along the length of the coating. In addition, some sections of the FPOL/PDMS (Applicator) fiber had no coating. This could have been due to the FPOL polymer having a lower molecular weight and lower viscosity than the HC polymer, thus requiring a greater amount of crosslinking in order to evenly bond to the fiber.

4.1.3. Ink Jet Coating

Ink jet coating was performed using the HC and NM_2A polymers as described in chapter 3.1.3. The amount of polymer that adhered to the fiber and the overall quality of polymer coating was dependant on both the type of polymer used and the ink jet parameters.

The HC (Ink Jet) fiber is shown in Figures 4-6 and 4-7. From Figure 4-6, it can be seen that the polymer tended to clump together and form a jagged non-uniform coating. An additional problem with the HC (Ink Jet) fiber was the polymer could not be fully crosslinked and bonded to the fused silica fiber since they were not mixed with the adhesive PDMS polymer. Images of the HC (Ink Jet) fiber taken before sampling (Figure 4-6) and after sampling (Figure 4-7) show the polymer was redistributed along the surface of the fiber. Migration of the polymer along the fiber may have occurred during desorption in the heated GC inlet. It is also possible the redistribution could be due to the polymer sticking to the inner walls of the needle assembly when retracted.

The NM_2A (Ink Jet) fiber was coated using a setting of 50 droplets per burst and 132 total bursts per layer. Figure 4-8 illustrates how the reduced number of drops per burst and increased spacing between bursts limited the degree of beading and clumping of the polymer. However, these settings resulted in only a very thin layer of polymer adhering to the surface of the fiber and some areas of the fiber remaining uncoated. This may also have been due to the type of polymer and the lower 0.4% concentration of NM_2A polymer in the ink jetting solution compared to the 1.0% concentration used with the HC polymer.

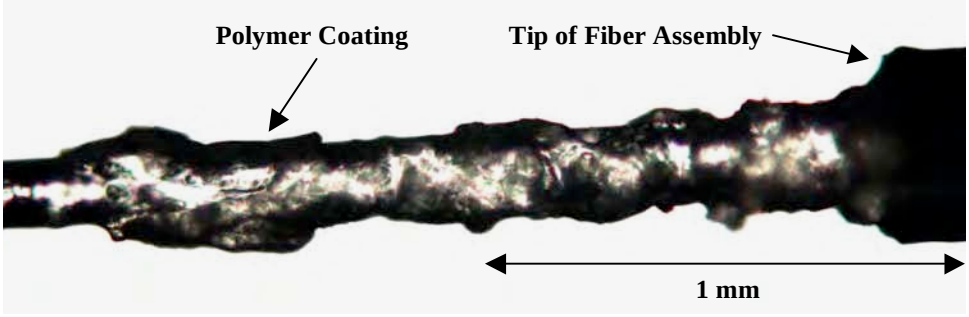


Figure 4-6. HC (Ink Jet) Fiber Before Sampling (10X Magnification)

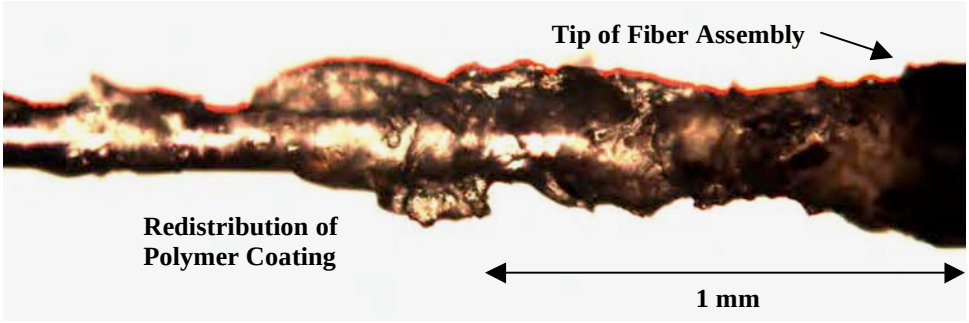


Figure 4-7. HC (Ink Jet) Fiber After Sampling (10X Magnification)

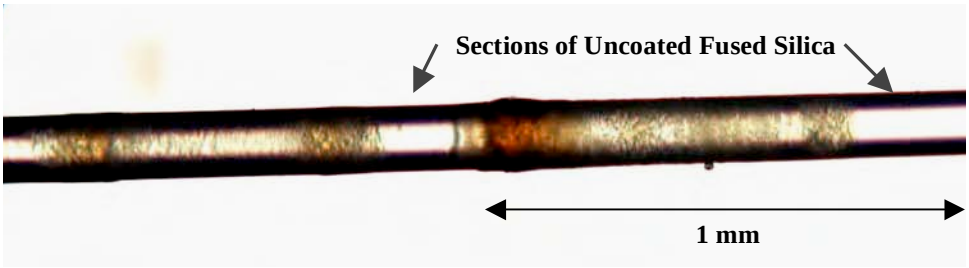


Figure 4-8. NM_2A (Ink Jet) Fiber (10X Magnification)

The NM_2A (Ink Jet) fiber coating did not exhibit any visible redistribution or degradation of its polymer coating after sampling as seen with the HC (Ink Jet) fiber. This could be due to the fiber having only a very thin polymer coating. It is also possible

that the increased molecular weight and presence of the napthyl groups within the polymer structure provided sufficient internal crosslinking of the polymer to increase its stability on the fiber.

Achieving a uniform polymer coating using the ink jet coating method may be possible with further testing and modification of the ink jet parameters. Adjusting the number of droplets per burst, the number of bursts per application layer, the number of layers, and continuous fiber rotation, should improve the quality of the coating. Other parameters that can be modified to possibly improve the coating process include the height of the spray nozzle above the fiber and the viscosity of the polymer solution. The use of higher molecular weight hydrogen bond acidic polymers, currently under development at the NRL, that exhibit more internal crosslinking may result in a more stable coating.

4.2. Vapor Phase Extraction

4.2.1. Vapor Phase Sampling Results

Vapor phase extraction of DMMP using static air sampling in tedlar bags was conducted as described in section 3.4. Chromatograms resulting from the 10 minute extractions of vapor phase DMMP at 0.5, 0.05, and 0.005 mg/m^3 using the HC/PDMS (Dipped#2) fiber are given in Figure 4-9. The chromatograms are characterized by the DMMP peak at approximately 4.6 minutes. As expected, the chromatograms show how the total DMMP peak area was reduced as the vapor phase concentration was lowered. The chromatograms for the other test fibers exhibited similar characteristics.

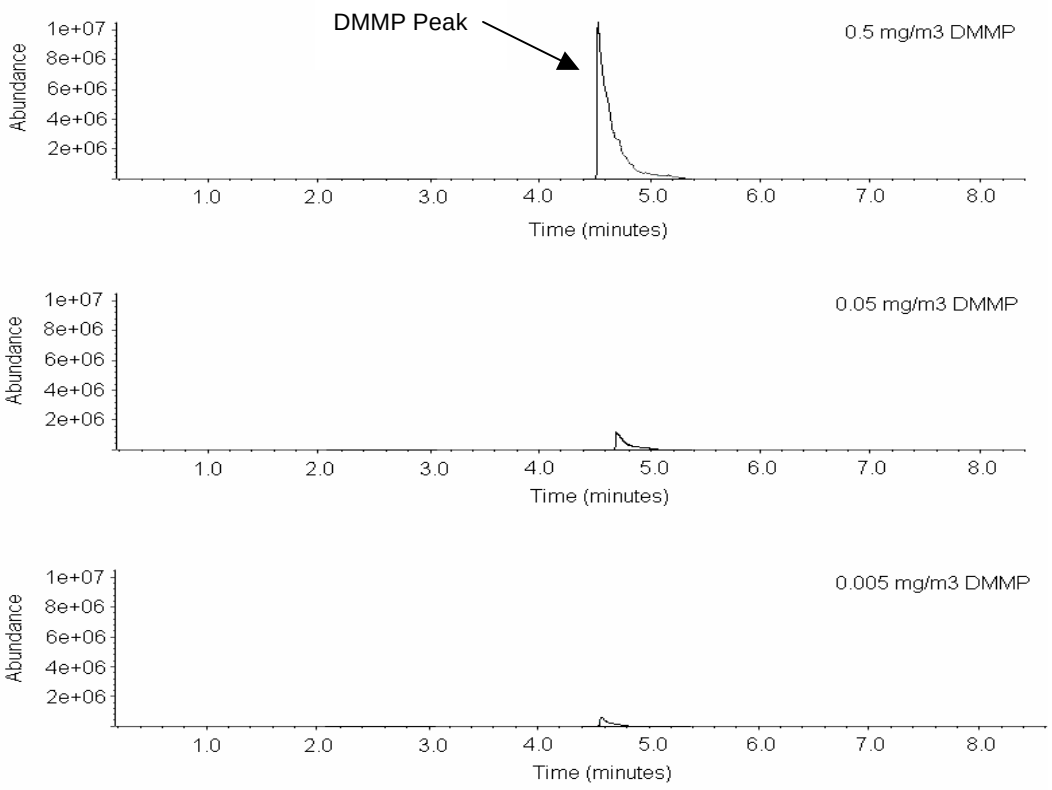


Figure 4-9. Total Ion Chromatograms for Vapor Phase DMMP Uptake at 0.5, 0.05, and 0.005 mg/m^3 Using Fiber HC/PDMS (Dipped#2)

Vapor phase DMMP uptake results comparing the total GC/MS peak area for each of the test fibers are shown graphically in Figures 4-10 and 4-11. In Figure 4-10 it can be seen that the HC/PDMS (Dipped#1 and #2) fibers, the HC (Ink Jet) fiber, and the commercial DVB/PDMS (65µm) fiber exhibited the highest total analyte uptake at both the 0.5 and 0.05 mg/m^3 sample concentrations. Results from these four fibers showed no statistical difference. The remaining fibers exhibited significantly lower ($p < 0.001$) total uptakes of DMMP.

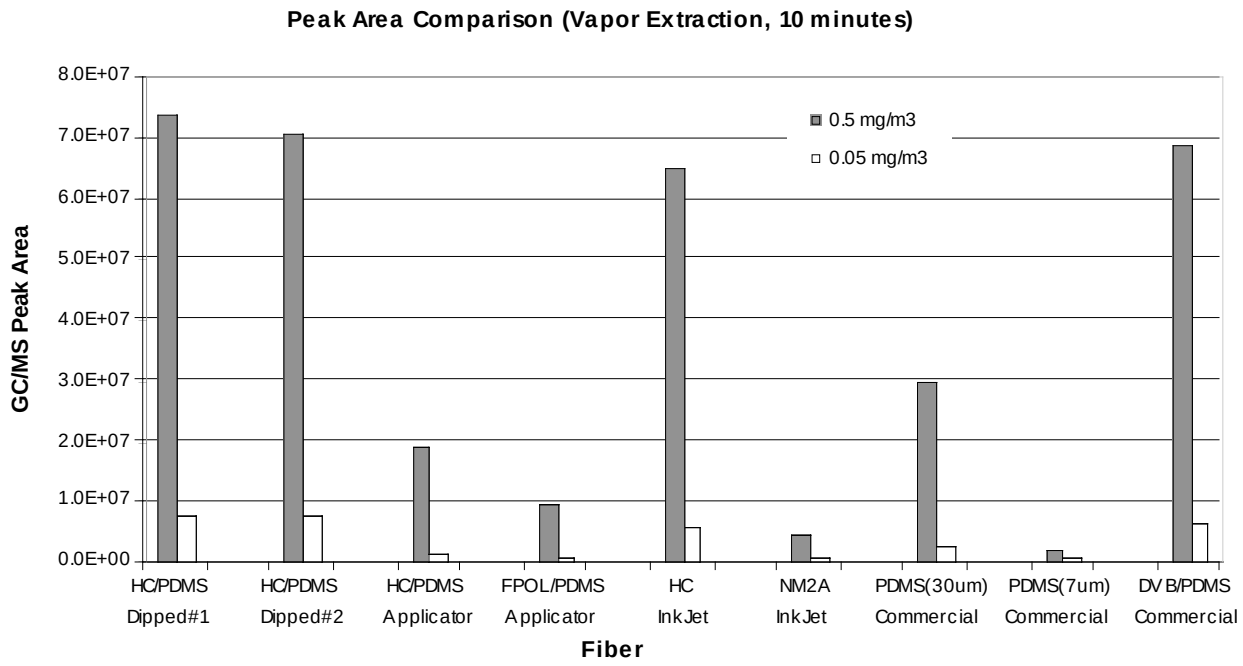


Figure 4-10. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at 0.5 and 0.05 mg/m^3

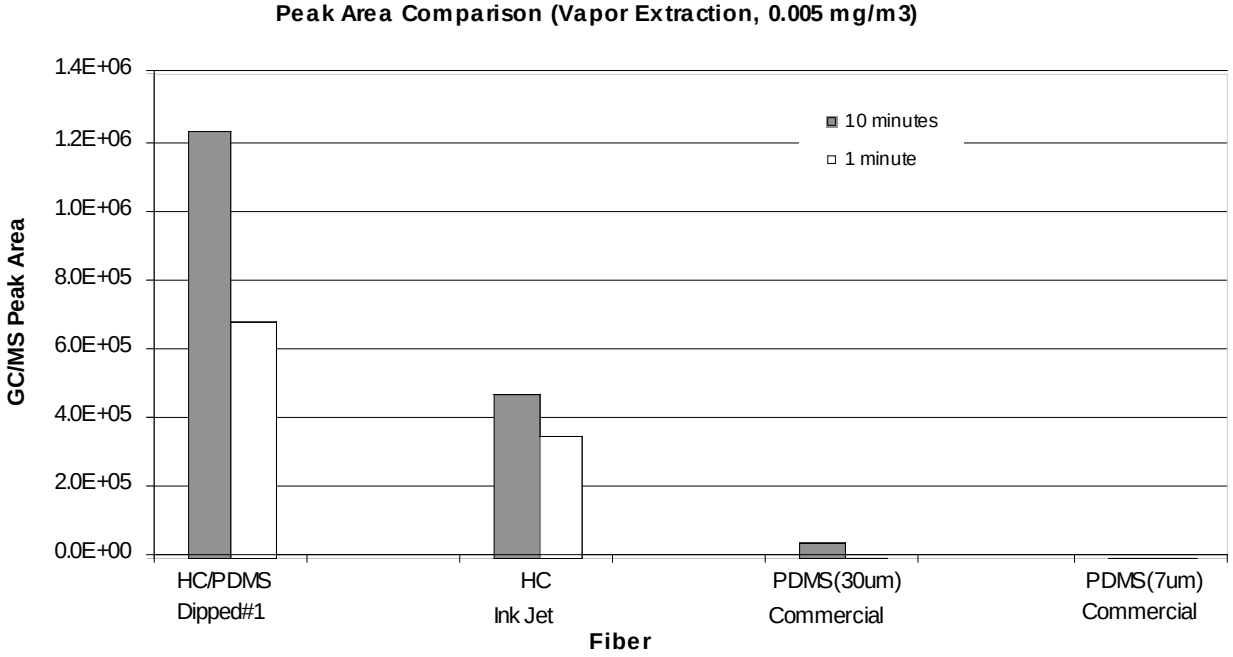


Figure 4-11. GC/MS Peak Area Comparison for Vapor Phase Extraction of DMMP at 0.005 mg/m^3

Figure 4-11 shows that the advantage in DMMP uptake of the HC/PDMS (Dipped#1) and HC (Ink Jet) fibers over the commercial PDMS fibers was even more pronounced at a concentration of 0.005 mg/m^3 for both 1 and 10 minute samples. (Note: the HC/PDMS (Dipped#2) fiber was physically damaged prior to sampling at 0.005 mg/m^3 and therefore could not be included in this part of the study.) For the 1 minute extraction at 0.005 mg/m^3, the PDMS (7μm) fiber did not detect the DMMP simulant, and the total GC/MS peak area for the PDMS (30μm) fiber was only about four times the background level. Neither of these fibers detected the DMMP at the 1 minute extraction. The HC/PDMS (Dipped#1) and HC (Ink Jet) fibers still exhibited large total GC/MS peak areas at both sampling times.

The total polymer volume of each of the test fibers is given in Figure 4-12. Due to the different polymer volumes on each of the test fibers, DMMP uptake was

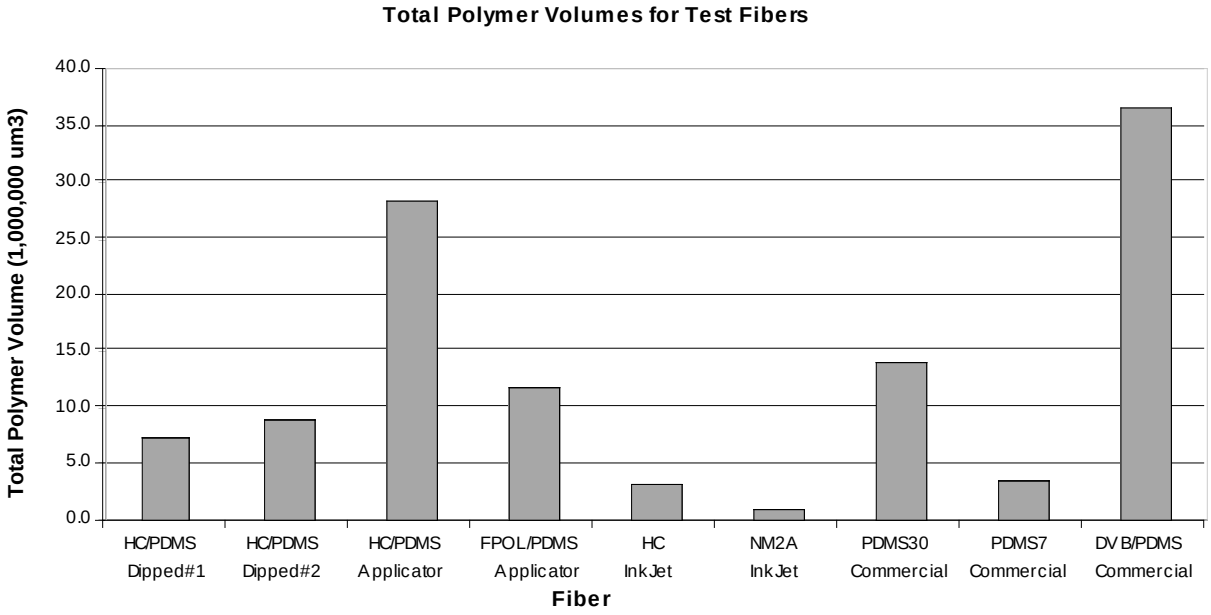


Figure 4-12. Total Polymer Volumes of Test Fibers

normalized by dividing the total GS/MS peak area by the polymer volume for each of the test fibers.

The total DMMP uptake per per μm^3 of polymer volume for each of the test fibers are shown graphically in Figures 4-13 and 4-14. Figure 4-13 shows the results from the 0.5 and 0.05 mg/m^3 sample concentrations. From this comparison, it can be seen that the HC (Ink Jet) fiber exhibited the greatest DMMP uptake per μm^3 of polymer volume, followed by the HC/PDMS (Dipped#1 and #2) fibers and then the NM_2A (Ink Jet) fiber. Both of the applicator coated fibers and the commercial fibers exhibited lower total uptakes relative to their polymer volumes.

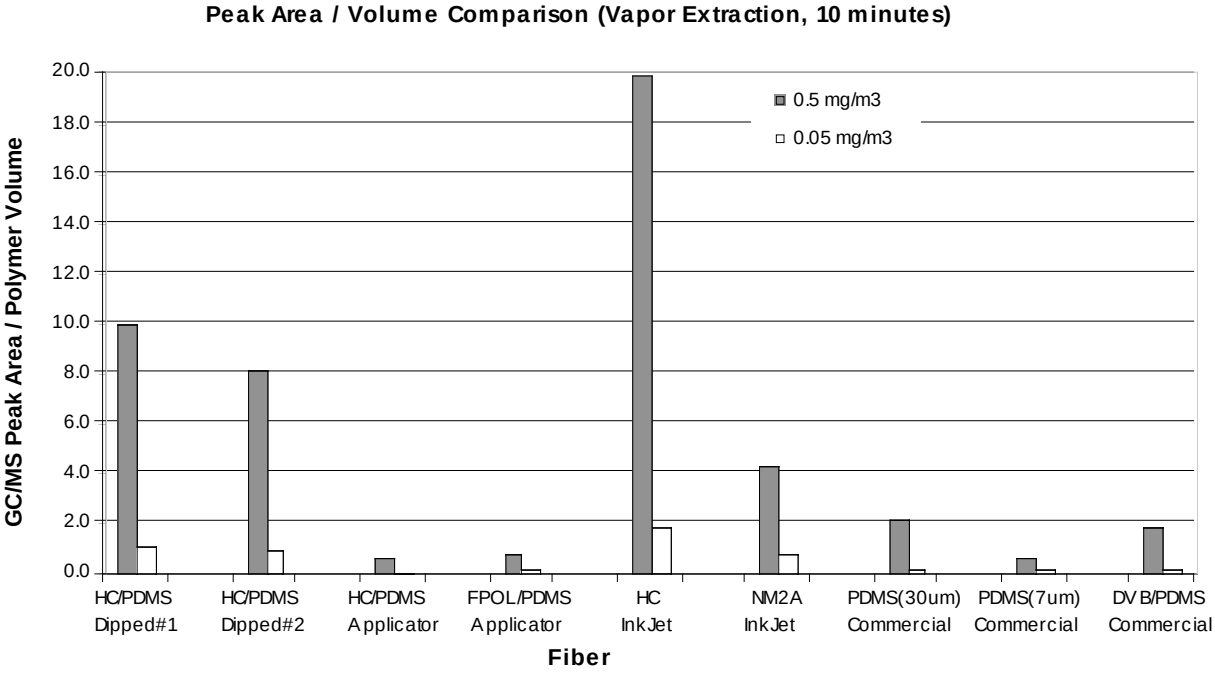


Figure 4-13. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of DMMP at 0.5 and 0.05 mg/m^3

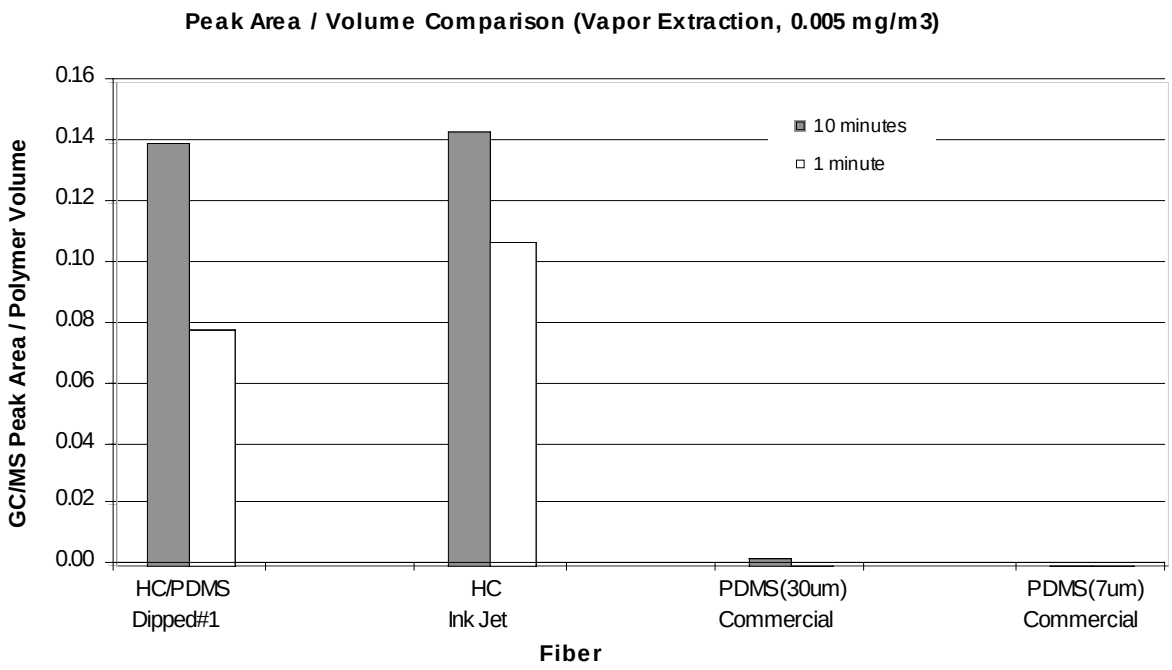


Figure 4-14. Peak Area/Polymer Volume Comparison for Vapor Phase Extraction of DMMP at 0.005 mg/m^3

Figure 4-14 illustrates the increased total DMMP uptake per um^3 of polymer volume of the HC/PDMS (Dipped#1) and HC (Ink Jet) fibers over both commercial PDMS fibers at a concentration of 0.005 mg/m^3 for both 1 and 10 minute samples. Again, this graph highlights increased performance of these two hydrogen bond acidic polymers over commercial PDMS at trace concentrations.

The data in Figures 4-13 and 4-14 also shows a significant difference in DMMP uptake per μm^3 of polymer volume between the HC/PDMS (Applicator) fiber compared to the HC/PDMS (Dipped#1 and #2) fibers. Although both types of fibers were coated with the same 50/50 mixture of HC and PDMS, the dip coated fibers performed much better than the applicator coated fiber. This indicates that the HC/PDMS mixture was effectively applied with dip coating but not with applicator coating. In addition, both the

dip coated and applicator coated HC/PDMS fibers exhibited polymer coatings that were clear prior to being cured. While the dip coated HC/PDMS polymer remained clear after being cured, both applicator coated fibers exhibited a visible change in the color and opacity of their polymer coatings. The applicator coated HC/PDMS polymer turned a golden color and the FPOL/PDMS polymer turned a light brown. This may be indicative of a change in the polymer chemistry brought about by the curing process. Curing the applicator coated polymers at a higher temperature of 200° C, may have caused thermal degradation of the HC and FPOL polymers which would lead to decreased amounts of DMMP being taken up. The NRL recommends a curing temperature of less than 150° C for these polymers. For future applicator coated fibers, lowering the curing temperature below 150° C may result in better performance.

An additional set of triplicate samples were taken using the HC/PDMS (Dipped#1 and #2) fibers and the two commercial PDMS fibers. This additional set was taken 8 days after the initial samples in order to determine if the HC/PDMS polymer mixture remained stable. It is possible that the PDMS would continue to polymerize with the HC, which would bind more reaction sites and inhibit analyte uptake. A significant difference was not observed between the two sample sets which suggests that the HC/PDMS mixture remained stable.

Results from the expected and actual average advantage in DMMP uptake of the hydrogen bond acidic polymers versus the PDMS (30μm) fiber are given in Table 4-1. Actual performance in DMMP uptake was calculated by comparing the total uptake per polymer volume ratios. At the 0.5 and 0.05 mg/m^3 concentrations, none of the hydrogen bond acidic polymers matched the expected performance advantage over the commercial

Expected and Actual Advantage in DMMP Uptake of Hydrogen Bond Acidic Polymers over PDMS for Vapor Phase Sampling (Comparison of Total Fiber Uptake Per Polymer Volume)				
Fiber	**Expected Advantage**	**Actual Advantage for Sampling Concentration**		
		0.5 mg/m3	**0.05 mg/m3**	**0.005 mg/m3**
HC/PDMS Dipped#1 and #2	10 fold	4.2	5.1	46.7
HC/PDMS Applicator	10 fold	None	None	(Not Sampled)
FPOL/PDMS Applicator	1.5 fold	None	None	(Not Sampled)
HC Ink jet	20 fold	9.4	9.2	48.0
NM2A Ink jet	10 fold	2.0	4.4	(Not Sampled)

Table 4-1. Expected and Actual Advantage in DMMP Uptake for Vapor Phase Extraction

PDMS (30µm) fiber. At the 0.005 mg/m^3 concentration, the amount of DMMP taken up by the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers was almost 50 times higher than the commercial PDMS (30µm) fiber. These results support previous research by the NRL that found that the advantage in analyte uptake of the hydrogen bond acidic polymers over commercial polymers tends to increase at lower concentrations.

The NM_2A (Ink Jet) fiber exhibited significantly higher levels of DMMP uptake over PDMS but did not meet expectations. Due to the very small quantity of polymer present on the NM_2A (Ink Jet) fiber, results may be more prone to measurement error. If a thicker layer of the NM_2A polymer could have been applied, the NM_2A (Ink Jet) fiber may have shown improved DMMP uptake results.

4.2.2. Data Analysis

In order to demonstrate repeatability in the sampling results, RSDs for all vapor phase sampling sets were calculated and are given in Figure 4-14. RSDs below 25% would generally be considered good repeatability for field sampling. All RSDs at both the 0.5 and 0.05 mg/m^3 concentrations were below 25%. Of the four fibers tested at the 0.005 mg/m^3 concentration, two of the fibers had RSDs above 25%, one remained below 25%, and the fourth fiber did not detect the DMMP simulant. This suggests that repeatable results were achieved for all of the fibers at the 0.5 and 0.05 mg/m^3 concentrations but, as the concentration was reduced to 0.005 mg/m^3, some of the fibers may have been approaching their lower detection limits, resulting in higher RSDs.

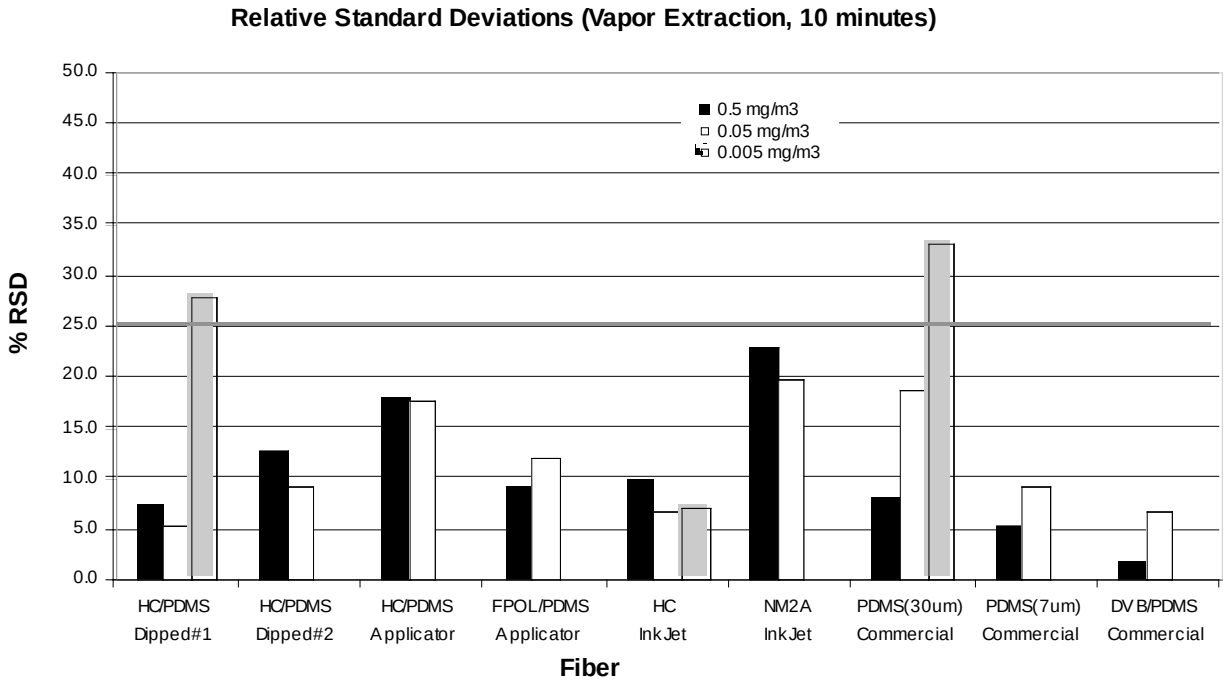


Figure 4-14. Relative Standard Deviations for Vapor Phase Extraction of DMMP

Data tables for all vapor phase extraction results are given in Appendix B. Statistical analysis of the data sets was performed using one-way ANOVA followed by Tukey HSD Post Hoc comparison. Statistical results are provided in Appendix C.

4.3. Aqueous Phase Extraction

4.3.1. Aqueous Phase Sampling Results

Aqueous phase extraction of DMMP using direct immersion water sampling in a glass vial was conducted as described in section 3.5. Total ion chromatograms resulting from the 10 minute extraction of aqueous phase DMMP at 100 and 1 ppm using the HC/PDMS (Dipped #2) fiber are given in Figure 4-15. The chromatograms are

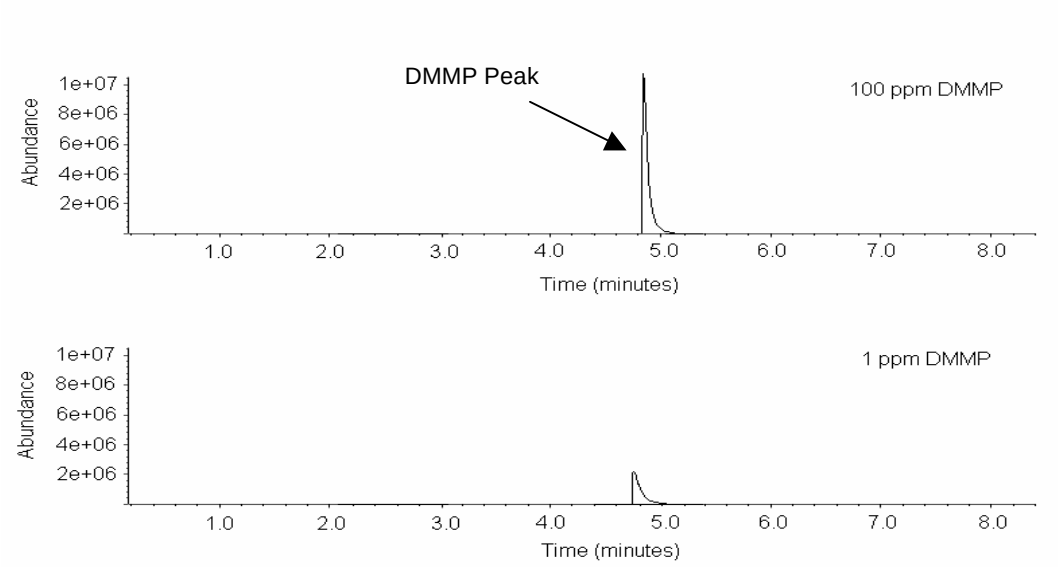


Figure 4-15. Total Ion Chromatogram for Aqueous Phase DMMP Uptake at 100 and 1 ppm Using Fiber HC/PDMS (Dipped#2)

characterized by the DMMP peak at approximately 4.8 minutes. As expected, the chromatograms show how the total DMMP peak area was reduced as the aqueous phase concentration was lowered. The chromatograms for the other test fibers exhibited similar characteristics.

DMMP uptake results for aqueous phase sampling are shown graphically in Figures 4-16 and 4-17. These graphs compare the average GC/MS peak area and the peak area per μm^3 of polymer volume for each of the test fibers. In Figure 4-16 it can be seen that the HC/PDMS (Dipped#1 and #2) fibers and the HC (Ink Jet) fiber had significantly greater ($p < 0.001$) total uptakes of DMMP than the remaining fibers for both the 100 and 1 ppm concentrations. The graph also clearly shows the large increase in the difference in uptake between the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers and the remaining fibers when the test concentration was lowered to 1 ppm. Decreasing

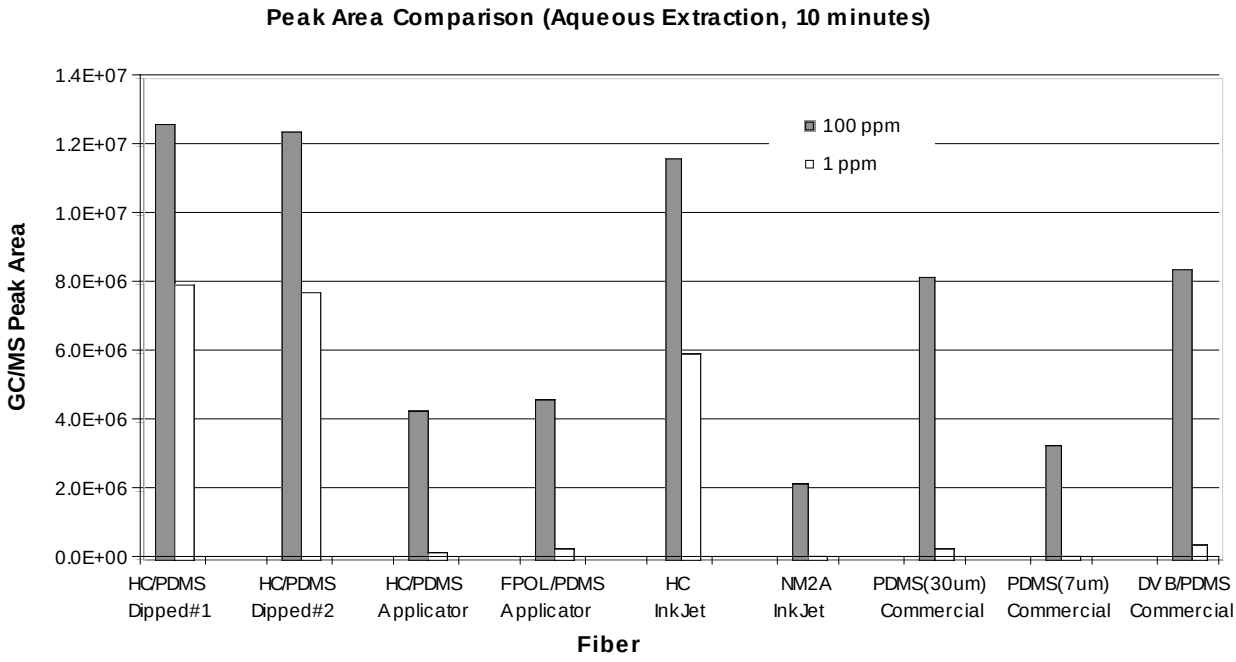


Figure 4-16. GC/MS Peak Area Comparison for Aqueous Phase Extraction of DMMP at 100 and 1 ppm

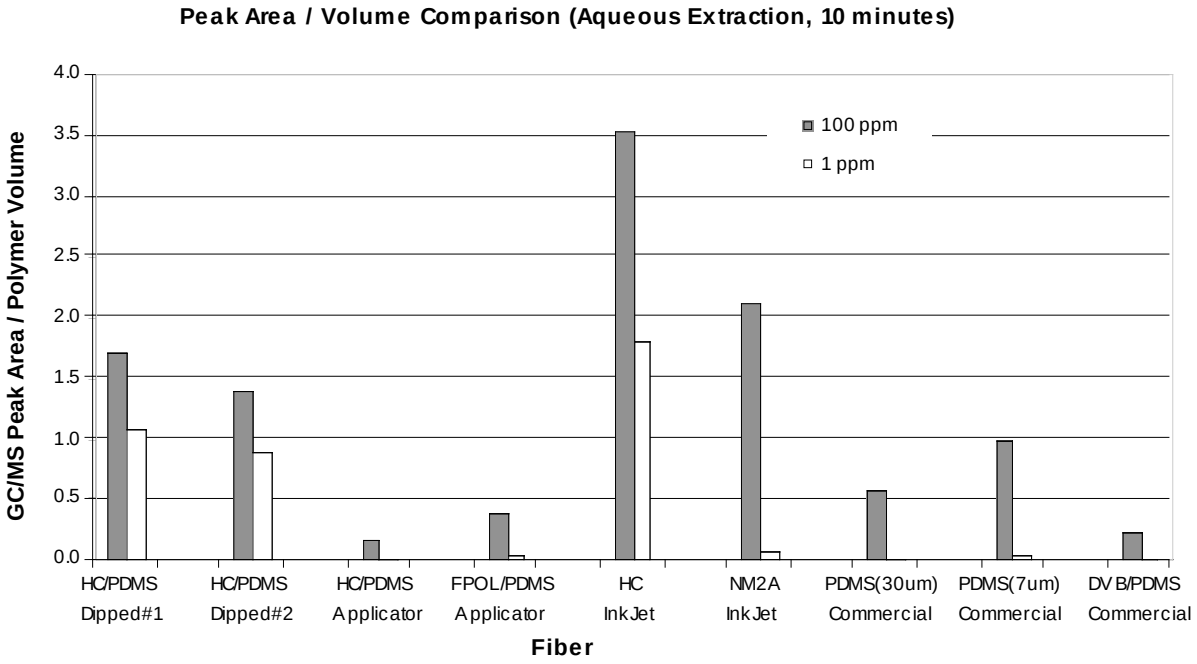


Table 4-17. GC/MS Peak Area/Polymer Volume Comparison for Aqueous Phase Extraction of DMMP at 100 and 1 ppm

the concentration from 100 ppm to 1 ppm reduced uptake in the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers by less than 50%. The remaining fibers exhibited a 93-96% decrease in DMMP uptake.

Figure 4-17 gives the DMMP uptake results per um^3 of polymer volume of each of the test fibers for both the 100 and 1 ppm sample concentrations. From this comparison, it can be seen that HC (Ink Jet) and HC/PDMS (Dipped #1 and #2) fibers exhibited a significantly greater ($p<0.001$) uptake per μm^3 of polymer volume than the commercial fibers. The NM_2A (Ink Jet) fiber also exhibited a significantly greater ($p<0.001$) DMMP uptake over all of the commercial fibers when polymer volume was taken into account. However, the NM_2A (Ink Jet) fiber performed much better at 100

ppm than at 1 ppm, which does not match the behavior of the other hydrogen bond acidic polymers.

Results from the expected and actual average advantage in DMMP uptake of the hydrogen bond acidic polymers versus the commercial PDMS (30μm) fiber are given in Table 4-5. Actual performance in DMMP uptake was calculated by comparing the total uptake per polymer volume ratios. At the 100 ppm concentration, none of the hydrogen bond acidic polymers matched the expected performance advantage. At the 1 ppm concentration, the amount of DMMP taken up by the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers was 42 and 79 times higher, respectively, than the commercial PDMS (30μm) fiber. As with the vapor phase sampling, these results support previous research by the NRL that found that the advantage in DMMP uptake of the hydrogen bond acidic polymers over commercial polymers tends to increase at lower concentrations.

Expected and Actual Advantage in Analyte Uptake of Hydrogen Bond Acidic Polymers over PDMS for Aqueous Phase Sampling (Comparison of Total Fiber Uptake Per Polymer Volume)			
Fiber	**Expected Advantage**	**Actual Advantage for Sampling Concentration**	
		100 ppm	**1 ppm**
HC/PDMS Dipped#1 and #2	10 fold	2.7	42.4
HC/PDMS Applicator	10 fold	None	None
FPOL/PDMS Applicator	1.5 fold	None	None
HC Ink jet	20 fold	6.1	78.9
NM2A Ink jet	10 fold	3.6	3.6

Table 4-5. Expected and Actual Advantage in DMMP Uptake for Aqueous Phase Extraction

The smaller difference seen at the 100 ppm concentration could have been due to the dip coated and ink jet coated fibers reaching equilibrium sooner than the commercial fibers due to their lower polymer volumes. It is possible that while uptake for the dip coated and ink jet coated fibers was restricted due to reaching equilibrium quickly, the fibers with a larger polymer volume continued to take up DMMP. The poor results for the applicator coated fibers again indicate the possibility of thermal degradation during the curing process.

4.3.2. Data Analysis

In order to demonstrate repeatability in the sampling results, RSDs for all aqueous phase sampling sets were calculated and are given in Figure 4-18. RSDs for all fibers

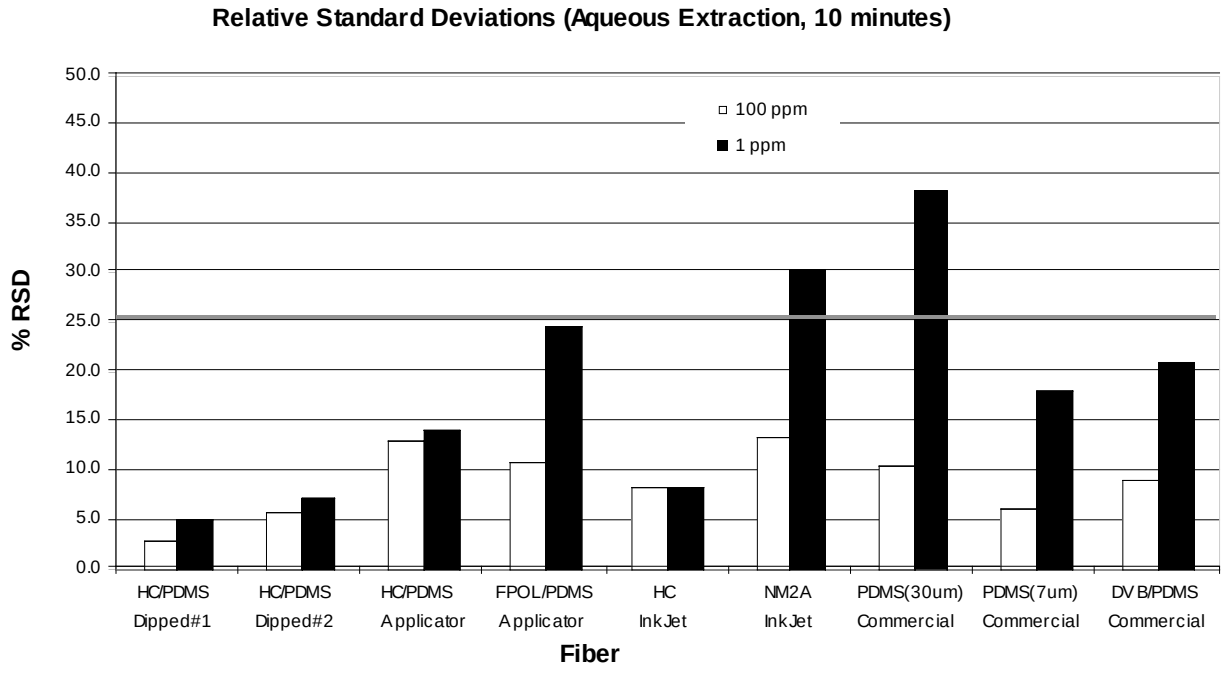


Figure 4-18. Relative Standard Deviations for Aqueous Phase Sampling of DMMP

were below 25% for the 100 ppm concentration. RSDs were higher for most of the fibers at the 1 ppm concentration with two fibers exceeding 25%. This suggests that reasonably repeatable results were achieved for all of the fibers at the 100 ppm concentration but, as the concentration was reduced to 1 ppm, some of the fibers may have been approaching their lower detection limits, resulting in higher RSDs. The RSDs for the HC/PDMS (Dipped#1 and #2) and HC (Ink Jet) fibers, however, remained below 9% even at the 1 ppm concentration as these fibers continued to collect significantly higher amounts of DMMP than the other fibers.

Data tables for all aqueous phase extraction results are given in Appendix B. Statistical analysis of all data sets were performed using one-way ANOVA followed by Tukey HSD Post Hoc comparison and are provided in Appendix C.

5. Conclusions

The focus of this research was to apply hydrogen bond acidic polymers to SPME. Three different methods of coating fused silica fibers with hydrogen bond acidic polymers were examined: dip coating, applicator coating and ink jet coating. Vapor and aqueous phase sampling of DMMP was accomplished to compare the uptake characteristics of hydrogen bond acidic coated SPME fibers to commercially manufactured SPME fibers. A summary of findings for each of the coating methods and each of the hydrogen bond acidic polymers is given in Table 5-1.

Summary of Hydrogen Bond Acid Polymer Coatings				
Fiber	**Uniform Coating**	**Bonded Coating**	**DMMP Uptake / Polymer Volume vs. PDMS**	**Notes**
HC/PDMS Dipped#1 and #2	No	Yes	Very Good	Little control over coating thickness
HC/PDMS Applicator	Yes	Yes	Poor	Possible thermal damage to coating
FPOL/PDMS Applicator	No	Yes	Poor	Possible thermal damage to coating
HC Ink Jet	No	No	Very Good	Redistribution of coating
NM2A Ink Jet	No	No	Good	Very thin coating

Table 5-1. Summary of Hydrogen Bond Acidic Polymer Coatings

The dip coating method was able to produce coatings that were fully hardened and bonded to the fused silica fiber when used in a 50/50 mixture with PDMS. These fibers exhibited very good DMMP uptake performance versus PDMS, especially at trace concentrations in both air and water. Uptake for these fibers was not as high as the HC

(Ink Jet) fiber due to the addition of the adhesive PDMS polymer which bonds with some of the active absorptive sites on the HC molecules. There was difficulty in producing a uniform polymer thickness with the dip coating method. Further experimentation with different dipping solution concentrations and modified fiber dipping and smoothing techniques may be able to improve control over the thickness and uniformity of the polymer coating.

The applicator coating method gave significantly more control over the thickness of the polymer coating and was able to produce bonded fibers of uniform thickness. The HC polymer showed more promise as it bonded more effectively than the FPOL polymer. A high curing temperature most likely caused polymer degradation, limiting the effectiveness of these fibers. The applicator coating method may become an effective method for producing bonded uniform coatings if curing temperatures are held below 150° C.

The ink jet coating method was able to provide a significant amount of control over the thickness of the polymer coating, but was not able to produce fibers of uniform thickness. Fine tuning the ink jet coating parameters should be able to produce a more uniform coating. The HC (Ink Jet) fiber exhibited the best performance in DMMP uptake, but since it was not hardened or bonded to the fused silica fiber, redistribution and possible degradation of the coating was observed. The NM_2A (Ink Jet) fiber exhibited only a slightly better performance over commercial PDMS but quantification of results was difficult due to the very limited volume of polymer on the fiber. The NM_2A polymer coating did appear more stable than the HC possibly due to its higher molecular

weight and ability to internally crosslink. Ink jet coating with other higher molecular weight polymers may produce more stable coatings.

As demonstrated by this study, hydrogen bond acidic polymers can be coated onto SPME fibers through several different methods. Sampling of nerve agent simulant shows the increased sensitivity of these polymers over current commercially available fibers, especially at trace concentrations in both vapor and aqueous media. This study showed the ability of hydrogen bond acidic SPME fibers to detect DMMP simulant at concentrations below nerve agent IDLH levels using rapid 1 to 10 minute sampling times. Detection of DMMP was demonstrated at 0.005 mg/m^3, where the IDLH level for sarin is 0.1 mg/m^3. The use of hydrogen bond acidic polymers in conjunction with SPME may provide significantly enhanced nerve agent sampling and detection for field operations.

5.1. Study Limitations

A limitation of this study was the fact that non-uniform polymer coatings required estimation of average polymer thickness. The use of fibers with significantly different polymer volumes also complicated direct comparison of analyte uptake between fibers. Another source of possible error is analyte losses to the test vial, syringe, or tedlar bag. Minor measurement errors may have occurred during preparation of standard solutions and injection of analyte into the test vials and tedlar bags. The use of a vapor standards generator may have been able to provide more accurate vapor concentrations. The limited availability of polymers also restricted the number of fibers that could be created and tested.

5.2. Additional Research

Hydrogen bond acidic polymers show great promise as a specialized polymer coating designed to adsorb trace levels of nerve agents in a field setting. Rapid field sampling may be greatly enhanced with the addition of these materials. This study was able to prove the concept but many more steps can be taken to optimize the hydrogen bond acidic SPME fibers and enhance their performance. Recommended follow-on research includes:

1. Applicator coating at a lower temperature: Reducing the curing temperature below 150° C during applicator coating may prevent polymer degradation and result in improved performance with a high quality coating. Successful modification of method parameters may result in the applicator coating method becoming a viable option for coating SPME fibers with hydrogen bond acidic polymers.

2. Optimization of ink jet coating parameters: Optimization of the ink jet coating parameters can be performed in order to consistently achieve a more uniform coating and an increased the ability to control the polymer thickness.

3. Varying the polymer mixture ratio: The 50/50 mixture of the HC polymer with PDMS produced a bonded and cured fiber coating. The percentage of PDMS may be able to be reduced to maximize the amount of HC in the mixture. An increased percentage of HC will result in a larger number of active –OH sites for analyte bonding and a higher sensitivity and selectivity. At the same time, the use of a higher

percentage of PDMS polymer with the lower viscosity FPOL polymer may result in better adherence of the polymer mixture to the fused silica fiber.

4. Polymer mixtures with PEHS: A poly-ethylhydrido siloxane (PEHS) polymer can be substituted for the adhesive PDMS polymer and mixed with the hydrogen bond acidic polymers. The PEHS has the advantage of having higher content of Si-H functional groups. These groups are used to crosslink the PEHS polymer and the hydrogen bond acidic polymer in the presence of the platinum catalyst. The PEHS should bind to the carbon chains of the HC polymer and not disturb the flouroalcohol groups needed for analyte uptake (Figure 5-1). This should increase crosslinking within the polymer mixture without sacrificing reaction sites on the HC molecules. In addition, it is possible that a smaller percentage of the PEHS would be needed to achieve the same amount of crosslinking provided by the PDMS.

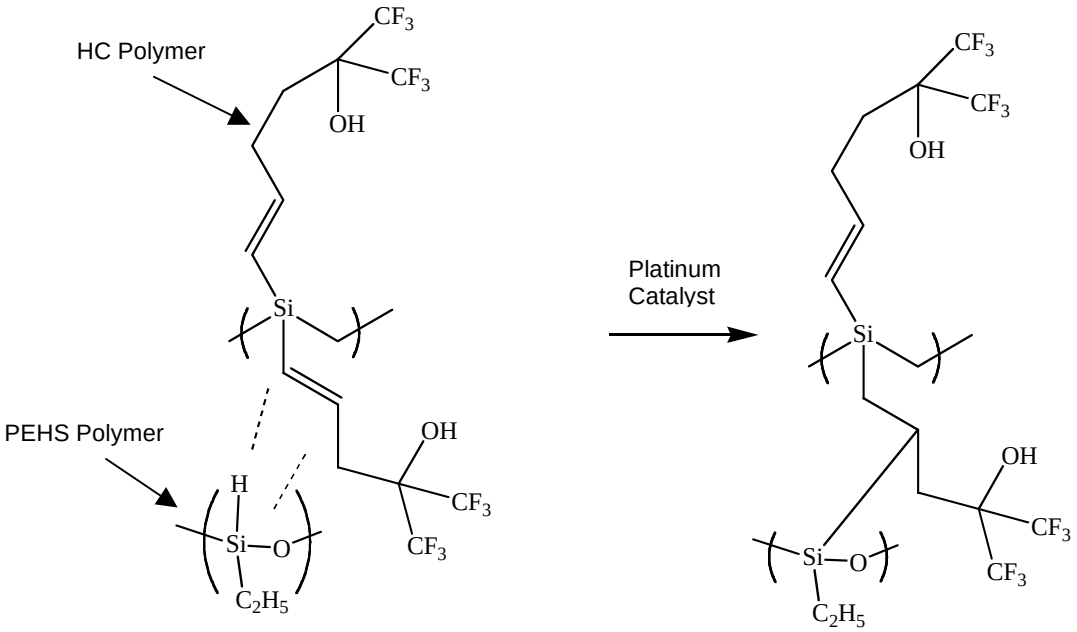


Figure 5-1. Reaction of PEHS with HC Polymer

5. Coating with linear higher molecular weight polymers: The NRL has also developed linear hydrogen bond acidic polycarbosilane polymers that have higher molecular weights than the hyperbranched HC, NM_2A, and FPOL polymers. These higher molecular weight polymers have the advantage of being significantly more viscous and should be easier to coat onto SPME fibers. They should also more readily crosslink and bind to the fused silica fiber. The use of these polymers may negate the need for adding a PDMS or PEHS polymer for additional crosslinking, allowing for an effective neat coating of the hydrogen bond acidic polymers.

6. Pre-treatment of fused silica fibers: Experimentation with a monomer primer can be conducted as a pretreatment for the uncoated fused silica fibers. Addition of the primer may provide a more favorable surface for attachment of the hydrogen bond acidic polymer and increase polymer binding.

7. Polymer uptake over time: The uptake of analyte over time for SPME fibers coated with hydrogen bond acidic polymers can be studied. Generating uptake curves over different sampling times will show the dynamics of analyte uptake over time and how long the fiber takes to reach equilibrium. This information will provide more comprehensive comparisons between different types of polymer coatings.

8. Limits of detection (LOD): This study has shown the effectiveness of hydrogen bond acidic polymers at a concentration of 0.005 mg/m^3. Follow-on studies using a vapor

standards generator can test even lower concentrations in order to establish an LOD for these polymers and the GC/MS analytical method.

9. Live agent testing: This study has shown the effectiveness of these polymers using nerve agent simulants. Further study using live G-series agent should be conducted to confirm the findings presented here.

Appendix A
Ink Jet Coating Parameters

Ink jet coating using the HC and NM_2A polymers was performed using a Jetlab II printing platform. The ink jet settings used in the creation of these fibers are provided below.

1. Ink jet coating settings for the HC (Ink Jet) fiber:

Parameter	Setting
Burst Rate	25-200 drops/burst
Rise	3 μs
Dwell	30 μs
Fall	3 μs
Echo Dwell	60 μs
Final Rise	3 μs
Dwell Voltage	40 V
Echo Voltage	-40 V
DC offset	0 V
Pattern	
x-direction	
Bursts	50-100
Burst separation	110-220 microns
Distance	11 mm
y-direction	
Bursts	2-3
Burst separation	83 microns
Distance	0.125-0.250 mm
Number of Passes	8 (4 per side)

2. Ink jet coating settings for the NM_2A (Ink Jet) fiber:

Parameter	Setting
Burst Rate	50 drops/burst
Rise	3 μs
Dwell	30 μs
Fall	3 μs
Echo Dwell	60 μs
Final Rise	3 μs
Dwell Voltage	40 V
Echo Voltage	-40 V
DC offset	0 V
Pattern	
x-direction	
Bursts	44
Burst separation	250 microns
Distance	11 mm
y-direction	
Bursts	3
Burst separation	83 microns
Distance	0.250 mm
Number of Passes	16 (8 per side)

Appendix B
DMMP Uptake Data Tables

DMMP uptake data for both vapor and aqueous phase sampling are provided below.

1. Vapor Phase Sampling

DMMP Uptake Data ($0.5\ mg/m^3$, static air sampling, 10 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#2)	6	73888517	7.5	7451465	9.92
HC/PDMS (Dipped#1)	6	70969258	12.7	8781697	8.08
HC/PDMS (Applicator)	3	19314537	18.1	28451049	0.68
FPOL/PDMS (Applicator)	3	9303526	9.4	11875220	0.78
HC (Ink Jet)	3	65202824	9.9	3284347	19.85
NM2A (Ink Jet)	3	4503001	22.8	1065000	4.23
PDMS (30um)	6	29701210	8.3	14038992	2.12
PDMS (7 um)	6	1907827	5.3	3417268	0.56
DVB/PDMS (65um),	3	68695351	1.8	36579920	1.88

DMMP Uptake Data ($0.05\ mg/m^3$, static air sampling, 10 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#2)	3	7941034	5.2	7451465	1.07
HC/PDMS (Dipped#1)	3	7529528	9.3	8781697	0.86
HC/PDMS (Applicator)	3	1688715	17.8	28451049	0.06
FPOL/PDMS (Applicator)	3	989133	12.1	11875220	0.08
HC (Ink Jet)	3	5791004	6.8	3284347	1.76
NM2A (Ink Jet)	3	891954	19.7	1065000	0.84
PDMS (30um)	3	2614003	18.7	14038992	0.19
PDMS (7 um)	3	494269	9.3	3417268	0.14
DVB/PDMS (65um),	3	6441191	6.8	36579920	0.18

DMMP Uptake Data (0.005 mg/m^3, static air sampling, 10 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#1)	3	1229887	27.9	8781697	0.140
HC (Ink Jet)	3	472256	7.3	3284347	0.144
PDMS (30um)	3	35614	33.1	14038992	0.003
PDMS (7 um)	3	Not detected	N/A	3417268	N/A

DMMP Uptake Data (0.005 mg/m^3, static air sampling, 1 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#1)	3	682417	12.8	8781697	0.08
HC (Ink Jet)	3	352213	5.8	3284347	0.11
PDMS (30um)	3	Not detected	N/A	14038992	N/A
PDMS (7 um)	3	Not detected	N/A	3417268	N/A

2. Aqueous Phase Sampling

DMMP Uptake Data (100 ppm, direct immersion water sampling, 10 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#2)	3	12615821	3.0	7451465	1.69
HC/PDMS (Dipped#1)	3	12369074	5.8	8781697	1.41
HC/PDMS (Applicator)	3	4279002	13.0	28451049	0.15
FPOL/PDMS (Applicator)	3	4680873	11.0	11875220	0.39
HC (Ink Jet)	3	11594812	8.3	3284347	3.53
NM2A (Ink Jet)	3	2250010	13.2	1065000	2.11
PDMS (30um)	3	8188440	10.6	14038992	0.58
PDMS (7 um)	3	3353670	6.3	3417268	0.98
DVB/PDMS (65um),	3	8371008	9.4	36579920	0.23

DMMP Uptake Data (1 ppm, direct immersion water sampling, 10 minutes)					
Fiber	# of Samples	Avgerage GC/MS Peak Area	RSD	Total Polymer Volume (um^3)	Peak Area / Volume
HC/PDMS (Dipped#2)	3	7941034	5.2	7451465	1.07
HC/PDMS (Dipped#1)	3	7767882	7.2	8781697	0.88
HC/PDMS (Applicator)	3	246134	14.1	28451049	0.01
FPOL/PDMS (Applicator)	3	322056	24.7	11875220	0.03
HC (Ink Jet)	3	5957670	8.2	3284347	1.81
NM2A (Ink Jet)	3	88420	30.2	1065000	0.08
PDMS (30um)	3	322151	38.4	14038992	0.02
PDMS (7 um)	3	144521	18.1	3417268	0.04
DVB/PDMS (65um),	3	424144	20.8	36579920	0.01

Appendix C
Statistical Comparisons

Statistical data comparing all sampling sets using one-way analysis of variance (ANOVA) followed by Tukey HSD Post Hoc comparison tests are provided below.

Total GC/MS Peak Area Comparisons (Vapor Phase, 0.5 mg/m^3, 10 Minutes)

ANOVA

PeakArea

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	34254044046292840.000	8	4281755505786605.000	206.239	.000
Within Groups	622832595081963.000	30	20761086502732.120		
Total	34876876641374800.000	38			

Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	27793383.833(*)	2630658.124	.000	19013562.01	36573205.65
	DVB/PDMS	-38994140.500(*)	3221885.046	.000	-49747182.25	-28241098.75
	HC/PDMS2	-44187306.500(*)	2630658.124	.000	-52967128.32	-35407484.68
	HC/PDMS3	-41268047.333(*)	2630658.124	.000	-50047869.15	-32488225.51
	HC/PDMS1	10386673.500	3221885.046	.065	-366368.25	21139715.25
	FPOL/PDMS	20397684.833(*)	3221885.046	.000	9644643.09	31150726.58
	HC	-35501613.833(*)	3221885.046	.000	-46254655.58	-24748572.09
	NMA	25198209.167(*)	3221885.046	.000	14445167.42	35951250.91
PDMS7	PDMS30	-27793383.833(*)	2630658.124	.000	-36573205.65	-19013562.01
	DVB/PDMS	-66787524.333(*)	3221885.046	.000	-77540566.08	-56034482.59
	HC/PDMS2	-71980690.333(*)	2630658.124	.000	-80760512.15	-63200868.51
	HC/PDMS3	-69061431.167(*)	2630658.124	.000	-77841252.99	-60281609.35
	HC/PDMS1	-17406710.333(*)	3221885.046	.000	-28159752.08	-6653668.59
	FPOL/PDMS	-7395699.000	3221885.046	.376	-18148740.75	3357342.75
	HC	-63294997.667(*)	3221885.046	.000	-74048039.41	-52541955.92
	NMA	-2595174.667	3221885.046	.996	-13348216.41	8157867.08
DVB/PDMS	PDMS30	38994140.500(*)	3221885.046	.000	28241098.75	49747182.25
	PDMS7	66787524.333(*)	3221885.046	.000	56034482.59	77540566.08
	HC/PDMS2	-5193166.000	3221885.046	.791	-15946207.75	5559875.75
	HC/PDMS3	-2273906.833	3221885.046	.998	-13026948.58	8479134.91
	HC/PDMS1	49380814.000(*)	3720312.398	.000	36964270.90	61797357.10
	FPOL/PDMS	59391825.333(*)	3720312.398	.000	46975282.24	71808368.43
	HC	3492526.667	3720312.398	.989	-8924016.43	15909069.76
	NMA	64192349.667(*)	3720312.398	.000	51775806.57	76608892.76
HC/PDMS2	PDMS30	44187306.500(*)	2630658.124	.000	35407484.68	52967128.32
	PDMS7	71980690.333(*)	2630658.124	.000	63200868.51	80760512.15
	DVB/PDMS	5193166.000	3221885.046	.791	-5559875.75	15946207.75
	HC/PDMS3	2919259.167	2630658.124	.968	-5860562.65	11699080.99
	HC/PDMS1	54573980.000(*)	3221885.046	.000	43820938.25	65327021.75
	FPOL/PDMS	64584991.333(*)	3221885.046	.000	53831949.59	75338033.08
	HC	8685692.667	3221885.046	.192	-2067349.08	19438734.41
	NMA	69385515.667(*)	3221885.046	.000	58632473.92	80138557.41
HC/PDMS3	PDMS30	41268047.333(*)	2630658.124	.000	32488225.51	50047869.15
	PDMS7	69061431.167(*)	2630658.124	.000	60281609.35	77841252.99
	DVB/PDMS	2273906.833	3221885.046	.998	-8479134.91	13026948.58

	HC/PDMS2	-2919259.167	2630658.124	.968	-11699080.99	5860562.65
	HC/PDMS1	51654720.833(*)	3221885.046	.000	40901679.09	62407762.58
	FPOL/PDMS	61665732.167(*)	3221885.046	.000	50912690.42	72418773.91
	HC	5766433.500	3221885.046	.688	-4986608.25	16519475.25
	NMA	66466256.500(*)	3221885.046	.000	55713214.75	77219298.25
HC/PDMS1	PDMS30	-10386673.500	3221885.046	.065	-21139715.25	366368.25
	PDMS7	17406710.333(*)	3221885.046	.000	6653668.59	28159752.08
	DVB/PDMS	-49380814.000(*)	3720312.398	.000	-61797357.10	-36964270.90
	HC/PDMS2	-54573980.000(*)	3221885.046	.000	-65327021.75	-43820938.25
	HC/PDMS3	-51654720.833(*)	3221885.046	.000	-62407762.58	-40901679.09
	FPOL/PDMS	10011011.333	3720312.398	.194	-2405531.76	22427554.43
	HC	-45888287.333(*)	3720312.398	.000	-58304830.43	-33471744.24
	NMA	14811535.667(*)	3720312.398	.010	2394992.57	27228078.76
FPOL/PDMS	PDMS30	-20397684.833(*)	3221885.046	.000	-31150726.58	-9644643.09
	PDMS7	7395699.000	3221885.046	.376	-3357342.75	18148740.75
	DVB/PDMS	-59391825.333(*)	3720312.398	.000	-71808368.43	-46975282.24
	HC/PDMS2	-64584991.333(*)	3221885.046	.000	-75338033.08	-53831949.59
	HC/PDMS3	-61665732.167(*)	3221885.046	.000	-72418773.91	-50912690.42
	HC/PDMS1	-10011011.333	3720312.398	.194	-22427554.43	2405531.76
	HC	-55899298.667(*)	3720312.398	.000	-68315841.76	-43482755.57
	NMA	4800524.333	3720312.398	.926	-7616018.76	17217067.43
HC	PDMS30	35501613.833(*)	3221885.046	.000	24748572.09	46254655.58
	PDMS7	63294997.667(*)	3221885.046	.000	52541955.92	74048039.41
	DVB/PDMS	-3492526.667	3720312.398	.989	-15909069.76	8924016.43
	HC/PDMS2	-8685692.667	3221885.046	.192	-19438734.41	2067349.08
	HC/PDMS3	-5766433.500	3221885.046	.688	-16519475.25	4986608.25
	HC/PDMS1	45888287.333(*)	3720312.398	.000	33471744.24	58304830.43
	FPOL/PDMS	55899298.667(*)	3720312.398	.000	43482755.57	68315841.76
	NMA	60699823.000(*)	3720312.398	.000	48283279.90	73116366.10
NMA	PDMS30	-25198209.167(*)	3221885.046	.000	-35951250.91	-14445167.42
	PDMS7	2595174.667	3221885.046	.996	-8157867.08	13348216.41
	DVB/PDMS	-64192349.667(*)	3720312.398	.000	-76608892.76	-51775806.57
	HC/PDMS2	-69385515.667(*)	3221885.046	.000	-80138557.41	-58632473.92
	HC/PDMS3	-66466256.500(*)	3221885.046	.000	-77219298.25	-55713214.75
	HC/PDMS1	-14811535.667(*)	3720312.398	.010	-27228078.76	-2394992.57
	FPOL/PDMS	-4800524.333	3720312.398	.926	-17217067.43	7616018.76
	HC	-60699823.000(*)	3720312.398	.000	-73116366.10	-48283279.90

* The mean difference is significant at the .05 level.

Peak Area Per Volume Comparisons (Vapor Phase, 0.5 mg/m^3, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1169.183	8	146.148	264.225	.000
Within Groups	16.594	30	.553		
Total	1185.776	38			

Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	1.5573333(*)	.4293864	.025	.124256	2.990411
	DVB/PDMS	.2376500	.5258888	1.000	-1.517504	1.992804
	HC/PDMS2	-7.8003667(*)	.4293864	.000	-9.233444	-6.367289
	HC/PDMS3	-5.9658667(*)	.4293864	.000	-7.398944	-4.532789
	HC/PDMS1	1.4367500	.5258888	.179	-.318404	3.191904
	FPOL/PDMS	1.3322167	.5258888	.257	-.422937	3.087371
	HC	-17.7370167(*)	.5258888	.000	-19.492171	-15.981863
	NMA	-2.1125500(*)	.5258888	.010	-3.867704	-.357396
PDMS7	PDMS30	-1.5573333(*)	.4293864	.025	-2.990411	-.124256
	DVB/PDMS	-1.3196833	.5258888	.267	-3.074837	.435471
	HC/PDMS2	-9.3577000(*)	.4293864	.000	-10.790777	-7.924623

	HC/PDMS3	-7.5232000(*)	.4293864	.000	-8.956277	-6.090123
	HC/PDMS1	-.1205833	.5258888	1.000	-1.875737	1.634571
	FPOL/PDMS	-.2251167	.5258888	1.000	-1.980271	1.530037
	HC	-19.2943500(*)	.5258888	.000	-21.049504	-17.539196
	NMA	-3.6698833(*)	.5258888	.000	-5.425037	-1.914729
DVB/PDMS	PDMS30	-.2376500	.5258888	1.000	-1.992804	1.517504
	PDMS7	1.3196833	.5258888	.267	-.435471	3.074837
	HC/PDMS2	-8.0380167(*)	.5258888	.000	-9.793171	-6.282863
	HC/PDMS3	-6.2035167(*)	.5258888	.000	-7.958671	-4.448363
	HC/PDMS1	1.1991000	.6072441	.571	-.827577	3.225777
	FPOL/PDMS	1.0945667	.6072441	.680	-.932111	3.121244
	HC	-17.9746667(*)	.6072441	.000	-20.001344	-15.947989
	NMA	-2.3502000(*)	.6072441	.014	-4.376877	-.323523
HC/PDMS2	PDMS30	7.8003667(*)	.4293864	.000	6.367289	9.233444
	PDMS7	9.3577000(*)	.4293864	.000	7.924623	10.790777
	DVB/PDMS	8.0380167(*)	.5258888	.000	6.282863	9.793171
	HC/PDMS3	1.8345000(*)	.4293864	.005	.401423	3.267577
	HC/PDMS1	9.2371167(*)	.5258888	.000	7.481963	10.992271
	FPOL/PDMS	9.1325833(*)	.5258888	.000	7.377429	10.887737
	HC	-9.9366500(*)	.5258888	.000	-11.691804	-8.181496
	NMA	5.6878167(*)	.5258888	.000	3.932663	7.442971
HC/PDMS3	PDMS30	5.9658667(*)	.4293864	.000	4.532789	7.398944
	PDMS7	7.5232000(*)	.4293864	.000	6.090123	8.956277
	DVB/PDMS	6.2035167(*)	.5258888	.000	4.448363	7.958671
	HC/PDMS2	-1.8345000(*)	.4293864	.005	-3.267577	-.401423
	HC/PDMS1	7.4026167(*)	.5258888	.000	5.647463	9.157771
	FPOL/PDMS	7.2980833(*)	.5258888	.000	5.542929	9.053237
	HC	-11.7711500(*)	.5258888	.000	-13.526304	-10.015996
	NMA	3.8533167(*)	.5258888	.000	2.098163	5.608471
HC/PDMS1	PDMS30	-1.4367500	.5258888	.179	-3.191904	.318404
	PDMS7	.1205833	.5258888	1.000	-1.634571	1.875737
	DVB/PDMS	-1.1991000	.6072441	.571	-3.225777	.827577
	HC/PDMS2	-9.2371167(*)	.5258888	.000	-10.992271	-7.481963
	HC/PDMS3	-7.4026167(*)	.5258888	.000	-9.157771	-5.647463
	FPOL/PDMS	-.1045333	.6072441	1.000	-2.131211	1.922144
	HC	-19.1737667(*)	.6072441	.000	-21.200444	-17.147089
	NMA	-3.5493000(*)	.6072441	.000	-5.575977	-1.522623
FPOL/PDMS	PDMS30	-1.3322167	.5258888	.257	-3.087371	.422937
	PDMS7	.2251167	.5258888	1.000	-1.530037	1.980271
	DVB/PDMS	-1.0945667	.6072441	.680	-3.121244	.932111
	HC/PDMS2	-9.1325833(*)	.5258888	.000	-10.887737	-7.377429
	HC/PDMS3	-7.2980833(*)	.5258888	.000	-9.053237	-5.542929
	HC/PDMS1	.1045333	.6072441	1.000	-1.922144	2.131211
	HC	-19.0692333(*)	.6072441	.000	-21.095911	-17.042556
	NMA	-3.4447667(*)	.6072441	.000	-5.471444	-1.418089
HC	PDMS30	17.7370167(*)	.5258888	.000	15.981863	19.492171
	PDMS7	19.2943500(*)	.5258888	.000	17.539196	21.049504
	DVB/PDMS	17.9746667(*)	.6072441	.000	15.947989	20.001344
	HC/PDMS2	9.9366500(*)	.5258888	.000	8.181496	11.691804
	HC/PDMS3	11.7711500(*)	.5258888	.000	10.015996	13.526304
	HC/PDMS1	19.1737667(*)	.6072441	.000	17.147089	21.200444
	FPOL/PDMS	19.0692333(*)	.6072441	.000	17.042556	21.095911
	NMA	15.6244667(*)	.6072441	.000	13.597789	17.651144
NMA	PDMS30	2.1125500(*)	.5258888	.010	.357396	3.867704
	PDMS7	3.6698833(*)	.5258888	.000	1.914729	5.425037
	DVB/PDMS	2.3502000(*)	.6072441	.014	.323523	4.376877
	HC/PDMS2	-5.6878167(*)	.5258888	.000	-7.442971	-3.932663
	HC/PDMS3	-3.8533167(*)	.5258888	.000	-5.608471	-2.098163
	HC/PDMS1	3.5493000(*)	.6072441	.000	1.522623	5.575977
	FPOL/PDMS	3.4447667(*)	.6072441	.000	1.418089	5.471444
	HC	-15.6244667(*)	.6072441	.000	-17.651144	-13.597789

* The mean difference is significant at the .05 level.

Total GC/MS Peak Area Comparisons (Vapor Phase, 0.05 mg/m^3, 10 Minutes)

ANOVA

PeakArea

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	287073006469922.100	8	35884125808740.260	131.125	.000
Within Groups	4925961484216.660	18	273664526900.926		
Total	291998967954138.800	26			

Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	2119733.333(*)	427133.490	.003	623116.50	3616350.16
	DVB/PDMS	-3827188.667(*)	427133.490	.000	-5323805.50	-2330571.84
	HC/PDMS2	-5976819.333(*)	427133.490	.000	-7473436.16	-4480202.50
	HC/PDMS3	-5632130.000(*)	427133.490	.000	-7128746.83	-4135513.17
	HC	-4935617.333(*)	427133.490	.000	-6432234.16	-3439000.50
	HC/PDMS1	925288.000	427133.490	.464	-571328.83	2421904.83
	FPOL/PDMS	1624870.000(*)	427133.490	.028	128253.17	3121486.83
	NMA	1722048.333(*)	427133.490	.017	225431.50	3218665.16
PDMS7	PDMS30	-2119733.333(*)	427133.490	.003	-3616350.16	-623116.50
	DVB/PDMS	-5946922.000(*)	427133.490	.000	-7443538.83	-4450305.17
	HC/PDMS2	-8096552.667(*)	427133.490	.000	-9593169.50	-6599935.84
	HC/PDMS3	-7751863.333(*)	427133.490	.000	-9248480.16	-6255246.50
	HC	-7055350.667(*)	427133.490	.000	-8551967.50	-5558733.84
	HC/PDMS1	-1194445.333	427133.490	.183	-2691062.16	302171.50
	FPOL/PDMS	-494863.333	427133.490	.956	-1991480.16	1001753.50
	NMA	-397685.000	427133.490	.988	-1894301.83	1098931.83
DVB/PDMS	PDMS30	3827188.667(*)	427133.490	.000	2330571.84	5323805.50
	PDMS7	5946922.000(*)	427133.490	.000	4450305.17	7443538.83
	HC/PDMS2	-2149630.667(*)	427133.490	.002	-3646247.50	-653013.84
	HC/PDMS3	-1804941.333(*)	427133.490	.012	-3301558.16	-308324.50
	HC	-1108428.667	427133.490	.254	-2605045.50	388188.16
	HC/PDMS1	4752476.667(*)	427133.490	.000	3255859.84	6249093.50
	FPOL/PDMS	5452058.667(*)	427133.490	.000	3955441.84	6948675.50
	NMA	5549237.000(*)	427133.490	.000	4052620.17	7045853.83
HC/PDMS2	PDMS30	5976819.333(*)	427133.490	.000	4480202.50	7473436.16
	PDMS7	8096552.667(*)	427133.490	.000	6599935.84	9593169.50
	DVB/PDMS	2149630.667(*)	427133.490	.002	653013.84	3646247.50
	HC/PDMS3	344689.333	427133.490	.995	-1151927.50	1841306.16
	HC	1041202.000	427133.490	.322	-455414.83	2537818.83
	HC/PDMS1	6902107.333(*)	427133.490	.000	5405490.50	8398724.16
	FPOL/PDMS	7601689.333(*)	427133.490	.000	6105072.50	9098306.16
	NMA	7698867.667(*)	427133.490	.000	6202250.84	9195484.50
HC/PDMS3	PDMS30	5632130.000(*)	427133.490	.000	4135513.17	7128746.83
	PDMS7	7751863.333(*)	427133.490	.000	6255246.50	9248480.16
	DVB/PDMS	1804941.333(*)	427133.490	.012	308324.50	3301558.16
	HC/PDMS2	-344689.333	427133.490	.995	-1841306.16	1151927.50
	HC	696512.667	427133.490	.777	-800104.16	2193129.50
	HC/PDMS1	6557418.000(*)	427133.490	.000	5060801.17	8054034.83
	FPOL/PDMS	7257000.000(*)	427133.490	.000	5760383.17	8753616.83
	NMA	7354178.333(*)	427133.490	.000	5857561.50	8850795.16
HC	PDMS30	4935617.333(*)	427133.490	.000	3439000.50	6432234.16
	PDMS7	7055350.667(*)	427133.490	.000	5558733.84	8551967.50
	DVB/PDMS	1108428.667	427133.490	.254	-388188.16	2605045.50
	HC/PDMS2	-1041202.000	427133.490	.322	-2537818.83	455414.83
	HC/PDMS3	-696512.667	427133.490	.777	-2193129.50	800104.16
	HC/PDMS1	5860905.333(*)	427133.490	.000	4364288.50	7357522.16
	FPOL/PDMS	6560487.333(*)	427133.490	.000	5063870.50	8057104.16
	NMA	6657665.667(*)	427133.490	.000	5161048.84	8154282.50
HC/PDMS1	PDMS30	-925288.000	427133.490	.464	-2421904.83	571328.83
	PDMS7	1194445.333	427133.490	.183	-302171.50	2691062.16
	DVB/PDMS	-4752476.667(*)	427133.490	.000	-6249093.50	-3255859.84
	HC/PDMS2	-6902107.333(*)	427133.490	.000	-8398724.16	-5405490.50

	HC/PDMS3	-6557418.000(*)	427133.490	.000	-8054034.83	-5060801.17
	HC	-5860905.333(*)	427133.490	.000	-7357522.16	-4364288.50
	FPOL/PDMS	699582.000	427133.490	.773	-797034.83	2196198.83
	NMA	796760.333	427133.490	.643	-699856.50	2293377.16
FPOL/PDMS	PDMS30	-1624870.000(*)	427133.490	.028	-3121486.83	-128253.17
	PDMS7	494863.333	427133.490	.956	-1001753.50	1991480.16
	DVB/PDMS	-5452058.667(*)	427133.490	.000	-6948675.50	-3955441.84
	HC/PDMS2	-7601689.333(*)	427133.490	.000	-9098306.16	-6105072.50
	HC/PDMS3	-7257000.000(*)	427133.490	.000	-8753616.83	-5760383.17
	HC	-6560487.333(*)	427133.490	.000	-8057104.16	-5063870.50
	HC/PDMS1	-699582.000	427133.490	.773	-2196198.83	797034.83
	NMA	97178.333	427133.490	1.000	-1399438.50	1593795.16
NMA	PDMS30	-1722048.333(*)	427133.490	.017	-3218665.16	-225431.50
	PDMS7	397685.000	427133.490	.988	-1098931.83	1894301.83
	DVB/PDMS	-5549237.000(*)	427133.490	.000	-7045853.83	-4052620.17
	HC/PDMS2	-7698867.667(*)	427133.490	.000	-9195484.50	-6202250.84
	HC/PDMS3	-7354178.333(*)	427133.490	.000	-8850795.16	-5857561.50
	HC	-6657665.667(*)	427133.490	.000	-8154282.50	-5161048.84
	HC/PDMS1	-796760.333	427133.490	.643	-2293377.16	699856.50
	FPOL/PDMS	-97178.333	427133.490	1.000	-1593795.16	1399438.50

* The mean difference is significant at the .05 level.

Peak Area Per Volume Comparisons (Vapor Phase, 0.05 mg/m^3, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	13.365	8	1.671	118.469	.000
Within Groups	.254	18	.014		
Total	13.618	26			

Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume
Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	.0415667	.0969585	1.000	-.298162	.381296
	DVB/PDMS	.0101000	.0969585	1.000	-.329629	.349829
	HC/PDMS2	-.9667000(*)	.0969585	.000	-1.306429	-.626971
	HC/PDMS3	-.7528333(*)	.0969585	.000	-1.092562	-.413104
	HC	-2.1125000(*)	.0969585	.000	-2.452229	-1.772771
	HC/PDMS1	.1268333	.0969585	.916	-.212896	.466562
	FPOL/PDMS	.1029333	.0969585	.973	-.236796	.442662
	NMA	-.6513333(*)	.0969585	.000	-.991062	-.311604
PDMS7	PDMS30	-.0415667	.0969585	1.000	-.381296	.298162
	DVB/PDMS	-.0314667	.0969585	1.000	-.371196	.308262
	HC/PDMS2	-1.0082667(*)	.0969585	.000	-1.347996	-.668538
	HC/PDMS3	-.7944000(*)	.0969585	.000	-1.134129	-.454671
	HC	-2.1540667(*)	.0969585	.000	-2.493796	-1.814338
	HC/PDMS1	.0852667	.0969585	.991	-.254462	.424996
	FPOL/PDMS	.0613667	.0969585	.999	-.278362	.401096
	NMA	-.6929000(*)	.0969585	.000	-1.032629	-.353171
DVB/PDMS	PDMS30	-.0101000	.0969585	1.000	-.349829	.329629
	PDMS7	.0314667	.0969585	1.000	-.308262	.371196
	HC/PDMS2	-.9768000(*)	.0969585	.000	-1.316529	-.637071
	HC/PDMS3	-.7629333(*)	.0969585	.000	-1.102662	-.423204
	HC	-2.1226000(*)	.0969585	.000	-2.462329	-1.782871
	HC/PDMS1	.1167333	.0969585	.945	-.222996	.456462
	FPOL/PDMS	.0928333	.0969585	.985	-.246896	.432562
	NMA	-.6614333(*)	.0969585	.000	-1.001162	-.321704
HC/PDMS2	PDMS30	.9667000(*)	.0969585	.000	.626971	1.306429
	PDMS7	1.0082667(*)	.0969585	.000	.668538	1.347996
	DVB/PDMS	.9768000(*)	.0969585	.000	.637071	1.316529
	HC/PDMS3	.2138667	.0969585	.442	-.125862	.553596
	HC	-1.1458000(*)	.0969585	.000	-1.485529	-.806071

	HC/PDMS1	1.0935333(*)	.0969585	.000	.753804	1.433262
	FPOL/PDMS	1.0696333(*)	.0969585	.000	.729904	1.409362
	NMA	.3153667	.0969585	.081	-.024362	.655096
HC/PDMS3	PDMS30	.7528333(*)	.0969585	.000	.413104	1.092562
	PDMS7	.7944000(*)	.0969585	.000	.454671	1.134129
	DVB/PDMS	.7629333(*)	.0969585	.000	.423204	1.102662
	HC/PDMS2	-.2138667	.0969585	.442	-.553596	.125862
	HC	-1.3596667(*)	.0969585	.000	-1.699396	-1.019938
	HC/PDMS1	.8796667(*)	.0969585	.000	.539938	1.219396
	FPOL/PDMS	.8557667(*)	.0969585	.000	.516038	1.195496
	NMA	.1015000	.0969585	.975	-.238229	.441229
HC	PDMS30	2.1125000(*)	.0969585	.000	1.772771	2.452229
	PDMS7	2.1540667(*)	.0969585	.000	1.814338	2.493796
	DVB/PDMS	2.1226000(*)	.0969585	.000	1.782871	2.462329
	HC/PDMS2	1.1458000(*)	.0969585	.000	.806071	1.485529
	HC/PDMS3	1.3596667(*)	.0969585	.000	1.019938	1.699396
	HC/PDMS1	2.2393333(*)	.0969585	.000	1.899604	2.579062
	FPOL/PDMS	2.2154333(*)	.0969585	.000	1.875704	2.555162
	NMA	1.4611667(*)	.0969585	.000	1.121438	1.800896
HC/PDMS1	PDMS30	-.1268333	.0969585	.916	-.466562	.212896
	PDMS7	-.0852667	.0969585	.991	-.424996	.254462
	DVB/PDMS	-.1167333	.0969585	.945	-.456462	.222996
	HC/PDMS2	-1.0935333(*)	.0969585	.000	-1.433262	-.753804
	HC/PDMS3	-.8796667(*)	.0969585	.000	-1.219396	-.539938
	HC	-2.2393333(*)	.0969585	.000	-2.579062	-1.899604
	FPOL/PDMS	-.0239000	.0969585	1.000	-.363629	.315829
	NMA	-.7781667(*)	.0969585	.000	-1.117896	-.438438
FPOL/PDMS	PDMS30	-.1029333	.0969585	.973	-.442662	.236796
	PDMS7	-.0613667	.0969585	.999	-.401096	.278362
	DVB/PDMS	-.0928333	.0969585	.985	-.432562	.246896
	HC/PDMS2	-1.0696333(*)	.0969585	.000	-1.409362	-.729904
	HC/PDMS3	-.8557667(*)	.0969585	.000	-1.195496	-.516038
	HC	-2.2154333(*)	.0969585	.000	-2.555162	-1.875704
	HC/PDMS1	.0239000	.0969585	1.000	-.315829	.363629
	NMA	-.7542667(*)	.0969585	.000	-1.093996	-.414538
NMA	PDMS30	.6513333(*)	.0969585	.000	.311604	.991062
	PDMS7	.6929000(*)	.0969585	.000	.353171	1.032629
	DVB/PDMS	.6614333(*)	.0969585	.000	.321704	1.001162
	HC/PDMS2	-.3153667	.0969585	.081	-.655096	.024362
	HC/PDMS3	-.1015000	.0969585	.975	-.441229	.238229
	HC	-1.4611667(*)	.0969585	.000	-1.800896	-1.121438
	HC/PDMS1	.7781667(*)	.0969585	.000	.438438	1.117896
	FPOL/PDMS	.7542667(*)	.0969585	.000	.414538	1.093996

* The mean difference is significant at the .05 level.

Total GC/MS Peak Area Comparisons (Vapor Phase, 0.005 mg/m^3, 10 Minutes)

ANOVA

PeakArea

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2190951569393.556	2	1095475784696.778	27.680	.001
Within Groups	237455809288.000	6	39575968214.667		
Total	2428407378681.555	8			

Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	HC/PDMS2	-1194273.667(*)	162431.459	.001	-1692657.99	-695889.35
	HC	-436642.000	162431.459	.080	-935026.32	61742.32
HC/PDMS2	PDMS30	1194273.667(*)	162431.459	.001	695889.35	1692657.99
	HC	757631.667(*)	162431.459	.008	259247.35	1256015.99
HC	PDMS30	436642.000	162431.459	.080	-61742.32	935026.32
	HC/PDMS2	-757631.667(*)	162431.459	.008	-1256015.99	-259247.35

* The mean difference is significant at the .05 level.

Peak Area Per Volume Comparisons (Vapor Phase, 0.005 mg/m^3, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.047	2	.023	31.561	.001
Within Groups	.004	6	.001		
Total	.051	8			

Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	HC/PDMS2	-.1625333(*)	.0222366	.001	-.230761	-.094305
	HC	-.1412333(*)	.0222366	.002	-.209461	-.073005
HC/PDMS2	PDMS30	.1625333(*)	.0222366	.001	.094305	.230761
	HC	.0213000	.0222366	.627	-.046928	.089528
HC	PDMS30	.1412333(*)	.0222366	.002	.073005	.209461
	HC/PDMS2	-.0213000	.0222366	.627	-.089528	.046928

* The mean difference is significant at the .05 level.

Total GC/MS Peak Area Comparisons (Aqueous Phase, 100 ppm, 10 Minutes)

ANOVA

PeakArea

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	392855357967250.700	8	49106919745906.300	121.488	.000
Within Groups	7275809252534.000	18	404211625140.778		
Total	400131167219784.700	26			

Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	4834769.667(*)	519109.253	.000	3015882.45	6653656.89
	DVB/PDMS	-182568.333	519109.253	1.000	-2001455.55	1636318.89
	HC/PDMS2	-4427381.333(*)	519109.253	.000	-6246268.55	-2608494.11
	HC/PDMS3	-4180634.333(*)	519109.253	.000	-5999521.55	-2361747.11
	HC/PDMS1	3909438.333(*)	519109.253	.000	2090551.11	5728325.55
	FPOL/PDMS	3507567.000(*)	519109.253	.000	1688679.78	5326454.22
	HC	-3406372.000(*)	519109.253	.000	-5225259.22	-1587484.78
	NMA	5938429.667(*)	519109.253	.000	4119542.45	7757316.89
PDMS7	PDMS30	-4834769.667(*)	519109.253	.000	-6653656.89	-3015882.45
	DVB/PDMS	-5017338.000(*)	519109.253	.000	-6836225.22	-3198450.78
	HC/PDMS2	-9262151.000(*)	519109.253	.000	-11081038.22	-7443263.78
	HC/PDMS3	-9015404.000(*)	519109.253	.000	-10834291.22	-7196516.78
	HC/PDMS1	-925331.333	519109.253	.692	-2744218.55	893555.89
	FPOL/PDMS	-1327202.667	519109.253	.270	-3146089.89	491684.55
	HC	-8241141.667(*)	519109.253	.000	-10060028.89	-6422254.45
	NMA	1103660.000	519109.253	.487	-715227.22	2922547.22
DVB/PDMS	PDMS30	182568.333	519109.253	1.000	-1636318.89	2001455.55
	PDMS7	5017338.000(*)	519109.253	.000	3198450.78	6836225.22
	HC/PDMS2	-4244813.000(*)	519109.253	.000	-6063700.22	-2425925.78
	HC/PDMS3	-3998066.000(*)	519109.253	.000	-5816953.22	-2179178.78
	HC/PDMS1	4092006.667(*)	519109.253	.000	2273119.45	5910893.89
	FPOL/PDMS	3690135.333(*)	519109.253	.000	1871248.11	5509022.55
	HC	-3223803.667(*)	519109.253	.000	-5042690.89	-1404916.45
	NMA	6120998.000(*)	519109.253	.000	4302110.78	7939885.22
HC/PDMS2	PDMS30	4427381.333(*)	519109.253	.000	2608494.11	6246268.55
	PDMS7	9262151.000(*)	519109.253	.000	7443263.78	11081038.22
	DVB/PDMS	4244813.000(*)	519109.253	.000	2425925.78	6063700.22
	HC/PDMS3	246747.000	519109.253	1.000	-1572140.22	2065634.22

	HC/PDMS1	8336819.667(*)	519109.253	.000	6517932.45	10155706.89
	FPOL/PDMS	7934948.333(*)	519109.253	.000	6116061.11	9753835.55
	HC	1021009.333	519109.253	.582	-797877.89	2839896.55
	NMA	10365811.000(*)	519109.253	.000	8546923.78	12184698.22
HC/PDMS3	PDMS30	4180634.333(*)	519109.253	.000	2361747.11	5999521.55
	PDMS7	9015404.000(*)	519109.253	.000	7196516.78	10834291.22
	DVB/PDMS	3998066.000(*)	519109.253	.000	2179178.78	5816953.22
	HC/PDMS2	-246747.000	519109.253	1.000	-2065634.22	1572140.22
	HC/PDMS1	8090072.667(*)	519109.253	.000	6271185.45	9908959.89
	FPOL/PDMS	7688201.333(*)	519109.253	.000	5869314.11	9507088.55
	HC	774262.333	519109.253	.846	-1044624.89	2593149.55
	NMA	10119064.000(*)	519109.253	.000	8300176.78	11937951.22
HC/PDMS1	PDMS30	-3909438.333(*)	519109.253	.000	-5728325.55	-2090551.11
	PDMS7	925331.333	519109.253	.692	-893555.89	2744218.55
	DVB/PDMS	-4092006.667(*)	519109.253	.000	-5910893.89	-2273119.45
	HC/PDMS2	-8336819.667(*)	519109.253	.000	-10155706.89	-6517932.45
	HC/PDMS3	-8090072.667(*)	519109.253	.000	-9908959.89	-6271185.45
	FPOL/PDMS	-401871.333	519109.253	.996	-2220758.55	1417015.89
	HC	-7315810.333(*)	519109.253	.000	-9134697.55	-5496923.11
	NMA	2028991.333(*)	519109.253	.022	210104.11	3847878.55
FPOL/PDMS	PDMS30	-3507567.000(*)	519109.253	.000	-5326454.22	-1688679.78
	PDMS7	1327202.667	519109.253	.270	-491684.55	3146089.89
	DVB/PDMS	-3690135.333(*)	519109.253	.000	-5509022.55	-1871248.11
	HC/PDMS2	-7934948.333(*)	519109.253	.000	-9753835.55	-6116061.11
	HC/PDMS3	-7688201.333(*)	519109.253	.000	-9507088.55	-5869314.11
	HC/PDMS1	401871.333	519109.253	.996	-1417015.89	2220758.55
	HC	-6913939.000(*)	519109.253	.000	-8732826.22	-5095051.78
	NMA	2430862.667(*)	519109.253	.005	611975.45	4249749.89
HC	PDMS30	3406372.000(*)	519109.253	.000	1587484.78	5225259.22
	PDMS7	8241141.667(*)	519109.253	.000	6422254.45	10060028.89
	DVB/PDMS	3223803.667(*)	519109.253	.000	1404916.45	5042690.89
	HC/PDMS2	-1021009.333	519109.253	.582	-2839896.55	797877.89
	HC/PDMS3	-774262.333	519109.253	.846	-2593149.55	1044624.89
	HC/PDMS1	7315810.333(*)	519109.253	.000	5496923.11	9134697.55
	FPOL/PDMS	6913939.000(*)	519109.253	.000	5095051.78	8732826.22
	NMA	9344801.667(*)	519109.253	.000	7525914.45	11163688.89
NMA	PDMS30	-5938429.667(*)	519109.253	.000	-7757316.89	-4119542.45
	PDMS7	-1103660.000	519109.253	.487	-2922547.22	715227.22
	DVB/PDMS	-6120998.000(*)	519109.253	.000	-7939885.22	-4302110.78
	HC/PDMS2	-10365811.000(*)	519109.253	.000	-12184698.22	-8546923.78
	HC/PDMS3	-10119064.000(*)	519109.253	.000	-11937951.22	-8300176.78
	HC/PDMS1	-2028991.333(*)	519109.253	.022	-3847878.55	-210104.11
	FPOL/PDMS	-2430862.667(*)	519109.253	.005	-4249749.89	-611975.45
	HC	-9344801.667(*)	519109.253	.000	-11163688.89	-7525914.45

* The mean difference is significant at the .05 level.

Peak Area Per Volume Comparisons (Aqueous Phase, 100 ppm, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	28.991	8	3.624	178.933	.000
Within Groups	.365	18	.020		
Total	29.355	26			

Post Hoc Multiple Comparisons

Dependent Variable: PeakAreaPerVolume

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	-.3981000	.1161964	.058	-.805236	.009036
	DVB/PDMS	.3544333	.1161964	.118	-.052703	.761570
	HC/PDMS2	-1.1098000(*)	.1161964	.000	-1.516936	-.702664
	HC/PDMS3	-.8252667(*)	.1161964	.000	-1.232403	-.418130
	HC/PDMS1	.4328667(*)	.1161964	.032	.025730	.840003

	FPOL/PDMS	.1891000	.1161964	.779	-.218036	.596236
	HC	-2.9470667(*)	.1161964	.000	-3.354203	-2.539930
	NMA	-1.5294333(*)	.1161964	.000	-1.936570	-1.122297
PDMS7	PDMS30	.3981000	.1161964	.058	-.009036	.805236
	DVB/PDMS	.7525333(*)	.1161964	.000	.345397	1.159670
	HC/PDMS2	-.7117000(*)	.1161964	.000	-1.118836	-.304564
	HC/PDMS3	-.4271667(*)	.1161964	.036	-.834303	-.020030
	HC/PDMS1	.8309667(*)	.1161964	.000	.423830	1.238103
	FPOL/PDMS	.5872000(*)	.1161964	.002	.180064	.994336
	HC	-2.5489667(*)	.1161964	.000	-2.956103	-2.141830
	NMA	-1.1313333(*)	.1161964	.000	-1.538470	-.724197
DVB/PDMS	PDMS30	-.3544333	.1161964	.118	-.761570	.052703
	PDMS7	-.7525333(*)	.1161964	.000	-1.159670	-.345397
	HC/PDMS2	-1.4642333(*)	.1161964	.000	-1.871370	-1.057097
	HC/PDMS3	-1.1797000(*)	.1161964	.000	-1.586836	-.772564
	HC/PDMS1	.0784333	.1161964	.999	-.328703	.485570
	FPOL/PDMS	-.1653333	.1161964	.875	-.572470	.241803
	HC	-3.3015000(*)	.1161964	.000	-3.708636	-2.894364
	NMA	-1.8838667(*)	.1161964	.000	-2.291003	-1.476730
HC/PDMS2	PDMS30	1.1098000(*)	.1161964	.000	.702664	1.516936
	PDMS7	.7117000(*)	.1161964	.000	.304564	1.118836
	DVB/PDMS	1.4642333(*)	.1161964	.000	1.057097	1.871370
	HC/PDMS3	.2845333	.1161964	.317	-.122603	.691670
	HC/PDMS1	1.5426667(*)	.1161964	.000	1.135530	1.949803
	FPOL/PDMS	1.2989000(*)	.1161964	.000	.891764	1.706036
	HC	-1.8372667(*)	.1161964	.000	-2.244403	-1.430130
	NMA	-.4196333(*)	.1161964	.040	-.826770	-.012497
HC/PDMS3	PDMS30	.8252667(*)	.1161964	.000	.418130	1.232403
	PDMS7	.4271667(*)	.1161964	.036	.020030	.834303
	DVB/PDMS	1.1797000(*)	.1161964	.000	.772564	1.586836
	HC/PDMS2	-.2845333	.1161964	.317	-.691670	.122603
	HC/PDMS1	1.2581333(*)	.1161964	.000	.850997	1.665270
	FPOL/PDMS	1.0143667(*)	.1161964	.000	.607230	1.421503
	HC	-2.1218000(*)	.1161964	.000	-2.528936	-1.714664
	NMA	-.7041667(*)	.1161964	.000	-1.111303	-.297030
HC/PDMS1	PDMS30	-.4328667(*)	.1161964	.032	-.840003	-.025730
	PDMS7	-.8309667(*)	.1161964	.000	-1.238103	-.423830
	DVB/PDMS	-.0784333	.1161964	.999	-.485570	.328703
	HC/PDMS2	-1.5426667(*)	.1161964	.000	-1.949803	-1.135530
	HC/PDMS3	-1.2581333(*)	.1161964	.000	-1.665270	-.850997
	FPOL/PDMS	-.2437667	.1161964	.503	-.650903	.163370
	HC	-3.3799333(*)	.1161964	.000	-3.787070	-2.972797
	NMA	-1.9623000(*)	.1161964	.000	-2.369436	-1.555164
FPOL/PDMS	PDMS30	-.1891000	.1161964	.779	-.596236	.218036
	PDMS7	-.5872000(*)	.1161964	.002	-.994336	-.180064
	DVB/PDMS	.1653333	.1161964	.875	-.241803	.572470
	HC/PDMS2	-1.2989000(*)	.1161964	.000	-1.706036	-.891764
	HC/PDMS3	-1.0143667(*)	.1161964	.000	-1.421503	-.607230
	HC/PDMS1	.2437667	.1161964	.503	-.163370	.650903
	HC	-3.1361667(*)	.1161964	.000	-3.543303	-2.729030
	NMA	-1.7185333(*)	.1161964	.000	-2.125670	-1.311397
HC	PDMS30	2.9470667(*)	.1161964	.000	2.539930	3.354203
	PDMS7	2.5489667(*)	.1161964	.000	2.141830	2.956103
	DVB/PDMS	3.3015000(*)	.1161964	.000	2.894364	3.708636
	HC/PDMS2	1.8372667(*)	.1161964	.000	1.430130	2.244403
	HC/PDMS3	2.1218000(*)	.1161964	.000	1.714664	2.528936
	HC/PDMS1	3.3799333(*)	.1161964	.000	2.972797	3.787070
	FPOL/PDMS	3.1361667(*)	.1161964	.000	2.729030	3.543303
	NMA	1.4176333(*)	.1161964	.000	1.010497	1.824770
NMA	PDMS30	1.5294333(*)	.1161964	.000	1.122297	1.936570
	PDMS7	1.1313333(*)	.1161964	.000	.724197	1.538470
	DVB/PDMS	1.8838667(*)	.1161964	.000	1.476730	2.291003
	HC/PDMS2	.4196333(*)	.1161964	.040	.012497	.826770
	HC/PDMS3	.7041667(*)	.1161964	.000	.297030	1.111303
	HC/PDMS1	1.9623000(*)	.1161964	.000	1.555164	2.369436
	FPOL/PDMS	1.7185333(*)	.1161964	.000	1.311397	2.125670
	HC	-1.4176333(*)	.1161964	.000	-1.824770	-1.010497

* The mean difference is significant at the .05 level.

Total GC/MS Peak Area Comparisons (Aqueous Phase, 1.0 ppm, 10 Minutes)

ANOVA

PeakArea

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	298481487143147.600	8	37310185892893.450	445.504	.000
Within Groups	1507467095970.667	18	83748171998.370		
Total	299988954239118.300	26			

Post Hoc Multiple Comparisons

Dependent Variable: PeakArea

Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	177630.333	236288.203	.997	-650290.94	1005551.60
	DVB/PDMS	-101993.333	236288.203	1.000	-929914.60	725927.94
	HC/PDMS2	-7618882.667(*)	236288.203	.000	-8446803.94	-6790961.40
	HC/PDMS3	-7445731.333(*)	236288.203	.000	-8273652.60	-6617810.06
	HC/PDMS1	76017.333	236288.203	1.000	-751903.94	903938.60
	FPOL/PDMS	95.000	236288.203	1.000	-827826.27	828016.27
	HC	-5635519.333(*)	236288.203	.000	-6463440.60	-4807598.06
	NMA	233731.333	236288.203	.982	-594189.94	1061652.60
PDMS7	PDMS30	-177630.333	236288.203	.997	-1005551.60	650290.94
	DVB/PDMS	-279623.667	236288.203	.950	-1107544.94	548297.60
	HC/PDMS2	-7796513.000(*)	236288.203	.000	-8624434.27	-6968591.73
	HC/PDMS3	-7623361.667(*)	236288.203	.000	-8451282.94	-6795440.40
	HC/PDMS1	-101613.000	236288.203	1.000	-929534.27	726308.27
	FPOL/PDMS	-177535.333	236288.203	.997	-1005456.60	650385.94
	HC	-5813149.667(*)	236288.203	.000	-6641070.94	-4985228.40
	NMA	56101.000	236288.203	1.000	-771820.27	884022.27
DVB/PDMS	PDMS30	101993.333	236288.203	1.000	-725927.94	929914.60
	PDMS7	279623.667	236288.203	.950	-548297.60	1107544.94
	HC/PDMS2	-7516889.333(*)	236288.203	.000	-8344810.60	-6688968.06
	HC/PDMS3	-7343738.000(*)	236288.203	.000	-8171659.27	-6515816.73
	HC/PDMS1	178010.667	236288.203	.997	-649910.60	1005931.94
	FPOL/PDMS	102088.333	236288.203	1.000	-725832.94	930009.60
	HC	-5533526.000(*)	236288.203	.000	-6361447.27	-4705604.73
	NMA	335724.667	236288.203	.876	-492196.60	1163645.94
HC/PDMS2	PDMS30	7618882.667(*)	236288.203	.000	6790961.40	8446803.94
	PDMS7	7796513.000(*)	236288.203	.000	6968591.73	8624434.27
	DVB/PDMS	7516889.333(*)	236288.203	.000	6688968.06	8344810.60
	HC/PDMS3	173151.333	236288.203	.997	-654769.94	1001072.60
	HC/PDMS1	7694900.000(*)	236288.203	.000	6866978.73	8522821.27
	FPOL/PDMS	7618977.667(*)	236288.203	.000	6791056.40	8446898.94
	HC	1983363.333(*)	236288.203	.000	1155442.06	2811284.60
	NMA	7852614.000(*)	236288.203	.000	7024692.73	8680535.27
HC/PDMS3	PDMS30	7445731.333(*)	236288.203	.000	6617810.06	8273652.60
	PDMS7	7623361.667(*)	236288.203	.000	6795440.40	8451282.94
	DVB/PDMS	7343738.000(*)	236288.203	.000	6515816.73	8171659.27
	HC/PDMS2	-173151.333	236288.203	.997	-1001072.60	654769.94
	HC/PDMS1	7521748.667(*)	236288.203	.000	6693827.40	8349669.94
	FPOL/PDMS	7445826.333(*)	236288.203	.000	6617905.06	8273747.60
	HC	1810212.000(*)	236288.203	.000	982290.73	2638133.27
	NMA	7679462.667(*)	236288.203	.000	6851541.40	8507383.94
HC/PDMS1	PDMS30	-76017.333	236288.203	1.000	-903938.60	751903.94
	PDMS7	101613.000	236288.203	1.000	-726308.27	929534.27
	DVB/PDMS	-178010.667	236288.203	.997	-1005931.94	649910.60
	HC/PDMS2	-7694900.000(*)	236288.203	.000	-8522821.27	-6866978.73
	HC/PDMS3	-7521748.667(*)	236288.203	.000	-8349669.94	-6693827.40
	FPOL/PDMS	-75922.333	236288.203	1.000	-903843.60	751998.94
	HC	-5711536.667(*)	236288.203	.000	-6539457.94	-4883615.40
	NMA	157714.000	236288.203	.999	-670207.27	985635.27
FPOL/PDMS	PDMS30	-95.000	236288.203	1.000	-828016.27	827826.27
	PDMS7	177535.333	236288.203	.997	-650385.94	1005456.60
	DVB/PDMS	-102088.333	236288.203	1.000	-930009.60	725832.94
	HC/PDMS2	-7618977.667(*)	236288.203	.000	-8446898.94	-6791056.40

	HC/PDMS3	-7445826.333(*)	236288.203	.000	-8273747.60	-6617905.06
	HC/PDMS1	75922.333	236288.203	1.000	-751998.94	903843.60
	HC	-5635614.333(*)	236288.203	.000	-6463535.60	-4807693.06
	NMA	233636.333	236288.203	.982	-594284.94	1061557.60
HC	PDMS30	5635519.333(*)	236288.203	.000	4807598.06	6463440.60
	PDMS7	5813149.667(*)	236288.203	.000	4985228.40	6641070.94
	DVB/PDMS	5533526.000(*)	236288.203	.000	4705604.73	6361447.27
	HC/PDMS2	-1983363.333(*)	236288.203	.000	-2811284.60	-1155442.06
	HC/PDMS3	-1810212.000(*)	236288.203	.000	-2638133.27	-982290.73
	HC/PDMS1	5711536.667(*)	236288.203	.000	4883615.40	6539457.94
	FPOL/PDMS	5635614.333(*)	236288.203	.000	4807693.06	6463535.60
	NMA	5869250.667(*)	236288.203	.000	5041329.40	6697171.94
NMA	PDMS30	-233731.333	236288.203	.982	-1061652.60	594189.94
	PDMS7	-56101.000	236288.203	1.000	-884022.27	771820.27
	DVB/PDMS	-335724.667	236288.203	.876	-1163645.94	492196.60
	HC/PDMS2	-7852614.000(*)	236288.203	.000	-8680535.27	-7024692.73
	HC/PDMS3	-7679462.667(*)	236288.203	.000	-8507383.94	-6851541.40
	HC/PDMS1	-157714.000	236288.203	.999	-985635.27	670207.27
	FPOL/PDMS	-233636.333	236288.203	.982	-1061557.60	594284.94
	HC	-5869250.667(*)	236288.203	.000	-6697171.94	-5041329.40

* The mean difference is significant at the .05 level.

Peak Area Per Volume Comparisons (Aqueous Phase, 1.0 ppm, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	10.430	8	1.304	391.706	.000
Within Groups	.060	18	.003		
Total	10.489	26			

Multiple Comparisons

Dependent Variable: PeakAreaPerVolume
Tukey HSD

(I) Fiber	(J) Fiber	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
PDMS30	PDMS7	-.0193333	.0471045	1.000	-.184381	.145714
	DVB/PDMS	.0113333	.0471045	1.000	-.153714	.176381
	HC/PDMS2	-1.0427667(*)	.0471045	.000	-1.207814	-.877719
	HC/PDMS3	-.8616333(*)	.0471045	.000	-1.026681	-.696586
	HC/PDMS1	.0142667	.0471045	1.000	-.150781	.179314
	FPOL/PDMS	-.0042000	.0471045	1.000	-.169248	.160848
	HC	-1.7910333(*)	.0471045	.000	-1.956081	-1.625986
	NMA	-.0601000	.0471045	.926	-.225148	.104948
PDMS7	PDMS30	.0193333	.0471045	1.000	-.145714	.184381
	DVB/PDMS	.0306667	.0471045	.999	-.134381	.195714
	HC/PDMS2	-1.0234333(*)	.0471045	.000	-1.188481	-.858386
	HC/PDMS3	-.8423000(*)	.0471045	.000	-1.007348	-.677252
	HC/PDMS1	.0336000	.0471045	.998	-.131448	.198648
	FPOL/PDMS	.0151333	.0471045	1.000	-.149914	.180181
	HC	-1.7717000(*)	.0471045	.000	-1.936748	-1.606652
	NMA	-.0407667	.0471045	.992	-.205814	.124281
DVB/PDMS	PDMS30	-.0113333	.0471045	1.000	-.176381	.153714
	PDMS7	-.0306667	.0471045	.999	-.195714	.134381
	HC/PDMS2	-1.0541000(*)	.0471045	.000	-1.219148	-.889052
	HC/PDMS3	-.8729667(*)	.0471045	.000	-1.038014	-.707919
	HC/PDMS1	.0029333	.0471045	1.000	-.162114	.167981
	FPOL/PDMS	-.0155333	.0471045	1.000	-.180581	.149514
	HC	-1.8023667(*)	.0471045	.000	-1.967414	-1.637319
	NMA	-.0714333	.0471045	.834	-.236481	.093614
HC/PDMS2	PDMS30	1.0427667(*)	.0471045	.000	.877719	1.207814
	PDMS7	1.0234333(*)	.0471045	.000	.858386	1.188481
	DVB/PDMS	1.0541000(*)	.0471045	.000	.889052	1.219148
	HC/PDMS3	.1811333(*)	.0471045	.025	.016086	.346181
	HC/PDMS1	1.0570333(*)	.0471045	.000	.891986	1.222081

	FPOL/PDMS	1.0385667(*)	.0471045	.000	.873519	1.203614
	HC	-.7482667(*)	.0471045	.000	-.913314	-.583219
	NMA	.9826667(*)	.0471045	.000	.817619	1.147714
HC/PDMS3	PDMS30	.8616333(*)	.0471045	.000	.696586	1.026681
	PDMS7	.8423000(*)	.0471045	.000	.677252	1.007348
	DVB/PDMS	.8729667(*)	.0471045	.000	.707919	1.038014
	HC/PDMS2	-.1811333(*)	.0471045	.025	-.346181	-.016086
	HC/PDMS1	.8759000(*)	.0471045	.000	.710852	1.040948
	FPOL/PDMS	.8574333(*)	.0471045	.000	.692386	1.022481
	HC	-.9294000(*)	.0471045	.000	-1.094448	-.764352
	NMA	.8015333(*)	.0471045	.000	.636486	.966581
HC/PDMS1	PDMS30	-.0142667	.0471045	1.000	-.179314	.150781
	PDMS7	-.0336000	.0471045	.998	-.198648	.131448
	DVB/PDMS	-.0029333	.0471045	1.000	-.167981	.162114
	HC/PDMS2	-1.0570333(*)	.0471045	.000	-1.222081	-.891986
	HC/PDMS3	-.8759000(*)	.0471045	.000	-1.040948	-.710852
	FPOL/PDMS	-.0184667	.0471045	1.000	-.183514	.146581
	HC	-1.8053000(*)	.0471045	.000	-1.970348	-1.640252
	NMA	-.0743667	.0471045	.804	-.239414	.090681
FPOL/PDMS	PDMS30	.0042000	.0471045	1.000	-.160848	.169248
	PDMS7	-.0151333	.0471045	1.000	-.180181	.149914
	DVB/PDMS	.0155333	.0471045	1.000	-.149514	.180581
	HC/PDMS2	-1.0385667(*)	.0471045	.000	-1.203614	-.873519
	HC/PDMS3	-.8574333(*)	.0471045	.000	-1.022481	-.692386
	HC/PDMS1	.0184667	.0471045	1.000	-.146581	.183514
	HC	-1.7868333(*)	.0471045	.000	-1.951881	-1.621786
	NMA	-.0559000	.0471045	.949	-.220948	.109148
HC	PDMS30	1.7910333(*)	.0471045	.000	1.625986	1.956081
	PDMS7	1.7717000(*)	.0471045	.000	1.606652	1.936748
	DVB/PDMS	1.8023667(*)	.0471045	.000	1.637319	1.967414
	HC/PDMS2	.7482667(*)	.0471045	.000	.583219	.913314
	HC/PDMS3	.9294000(*)	.0471045	.000	.764352	1.094448
	HC/PDMS1	1.8053000(*)	.0471045	.000	1.640252	1.970348
	FPOL/PDMS	1.7868333(*)	.0471045	.000	1.621786	1.951881
	NMA	1.7309333(*)	.0471045	.000	1.565886	1.895981
NMA	PDMS30	.0601000	.0471045	.926	-.104948	.225148
	PDMS7	.0407667	.0471045	.992	-.124281	.205814
	DVB/PDMS	.0714333	.0471045	.834	-.093614	.236481
	HC/PDMS2	-.9826667(*)	.0471045	.000	-1.147714	-.817619
	HC/PDMS3	-.8015333(*)	.0471045	.000	-.966581	-.636486
	HC/PDMS1	.0743667	.0471045	.804	-.090681	.239414
	FPOL/PDMS	.0559000	.0471045	.949	-.109148	.220948
	HC	-1.7309333(*)	.0471045	.000	-1.895981	-1.565886

* The mean difference is significant at the .05 level.

Comparisons of Dip Coated Fiber Sampling 8-Day Repeat Sampling

(VaporPhase, 1.0 ppm, 10 Minutes)

ANOVA

PeakAreaPerVolume

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	11716119082008.390	1	11716119082008.390	.283	.606
Within Groups	41395607648399.330	10	41395607648399.330		
Total	42567219556601.600	11			

Bibliography

Bryant, C.K. Uniformed Services University of the Health Sciences Thesis: "Chemical Agent Identification Using Field-Based Attenuated Total Reflectance Infrared Detection and Solid Phase Microextraction", June 2006.

Department of the Army. Memorandum, Subject: "Implementation Guidance Policy for Airborne Exposure Limits for GB, GA, GD, GF, VX, H, HD, and HT". 18 June 2004.

Grate, Jay W.; Patrash, Samuel J.; Kaganove, Steven N. "Hydrogen Bond Acidic Polymers for Surface Acoustic Wave Vapor Sensors and Arrays". *Analytical Chemistry*, 1999, 71, 5: 1033-1040.

Harvey, S.D.; Nelson, D.A; Wright, B.W.; Grate, J.W. "Selective Stationary Phase for Solid-Phase Microextraction Analysis of Sarin (GB)". *Journal of Chromatography*, 2002, 954: 217-225.

Hauser, Eric J.; Simonson, Duane L.; Stepnowski, Jennifer L.; Ross, Stuart K.; Stepnowski, Stanley V.; McGill, R. Andrew. "Design of Hydrogen Bond Acidic Polycarbosilanes for Chemical Sensor Applications." *Polymer Preprints*, 2004, 45(1): 541-542.

Hook, Gray L.; Kimm, Gregory; Koch, David; Savage, Paul B; Ding, Bangwei; Smith, Philip A. "Detection of VX Contamination in Soil Through Solid-Phase Microextraction Sampling and Gas Chromatography/Mass Spectrometry of the VX Degradation Product Bis(diisopropylaminoethyl)disulfide. *Journal of Chromatography*, 2003, 992: 1-9.

Hook, Gary L; Kimm Gregory; Betsinger, Geoffrey; Savage, Paul B.; Swift, Austin; Logan, Tom; Smith, Philip A. "Solid Phase Microextraction Sampling and Gas Chromatography/Mass Spectrometry for Field Detection of the Chemical Warfare Agent O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)." *Journal of Separation Science*, 2003, 26: 1091-1096.

Hook, Gary L.; Jackson Lapage, Carmela; Miller, Stephen I; Smith, Philip A. "Dynamic Solid-Phase Microextraction for Sampling of Airborne Sarin with Gas Chromatography-Mass Spectrometry for Rapid Field Detection and Quantification". *Journal of Separation Science*, 2004, 27: 1017-1022.

Kimm, Gregory L.; Hook, Gary L.; Smith, Philip A. "Application of Headspace Solid-Phase Microextraction and Gas Chromatography-Mass Spectrometry for Detection of the Chemical Warfare Agent Bis(2-chloroethyl)sulfide in Soil. *Journal of Chromatography*, 2002, 971: 185-191.

Lakso, H.-A. and Ng, W.F. "Determination of Chemical Warfare Agents in Natural Water Samples by Solid Phase Microextraction." *Analytical Chemistry,* 1997, 69: 1866-1872.

McCafferty, R.R. and Lennarson, P.J. “Common Chemical Agent Threats” *Neurosurgery,* 2002, 12, 3.

Naval Research Laboratory (NRL). SPME-Polymer Meeting: 13 Feb 2006. U.S. Naval Research Laboratory, Washington D.C.

Pawliszyn, J. Solid Phase Microextraction Theory and Practice. New York, Wiley-VCH Inc., 1997.

Pawliszyn, J. Applications of Solid Phase Microextraction. Hertfordshire, Royal Society of Chemistry, 1999.

Schneider, J. F.; Bopari, A. S.; Reed, L. L "Screening for Sarin in Air and Water by Solid Phase Microextraction - Gas Chromatography - Mass Spectrometry." *Journal of Chromatographic Science,* 1999, 39: 420-424.

Smith, Philip A.; Jackson Lepage, Carmela R.; Koch, David; Wyatt, Haley D.M.; Hook, Gary L.; Betsinger, Geoffrey; Erickson, Richard P.; Eckenrode, Brian A. “Detection of Gas Phase Chemical Warfare Agents Using Field-Portable Gas Chromatography-Mass Spectrometry Systems: Instrument and Sampling Strategy Considerations”. *Trends in Analytical Chemistry*, 2004, 23, 4: 296.

Sun, Y. and Ong, K. Detection Technologies for Chemical Warfare Agents. Boca Raton, CRC Press, 2005. 16-20.

U.S. Department of State. Bureau of International Security and Nonproliferation. “Combating WMD Terrorism: WMD Terrorism Risk”, 2006, http://www.state.gov/t/isn/c16585.htm.

Curriculum Vitae

Capt Stephen L. Boglarski graduated from Rensselear Polytechnic Institute in 1996 with a Bachelor of Science in Environmental Engineering. He served as a Chief, Industrial Hygiene Element at Vandenberg AFB from 1997-1999 where he supported space and missile launch operations for the Western Range and managed the health risk assessment and surveillance program affecting over 300 workplaces and over 3500 workers and. While stationed at Osan AB from 1999-2000 he served as OIC, Occupational and Environmental Readiness and as Base Radiation Safety Officer. From 2001-2005, he served as Chief, Bioenvironmental Engineering at Hanscom AFB and was recognized as the U.S. Air Force Company Grade Bioenvironmental Engineer of the Year for 2001. In 2005, he entered the Graduate School of Biomedical Sciences and Public Health, Uniformed Services University. Upon graduation in Jun 2006, he will be assigned as Chief, Bioenvironmental Engineering at Ellsworth AFB.